Nanoparticle-Based Sustainable Agriculture and Food Science: Recent Advances and Future Outlook

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In the current scenario, it is an urgent requirement to satisfy the nutritional demands of the rapidly growing global population. Using conventional farming, nearly one third of crops get damaged, mainly due to pest infestation, microbial attacks, natural disasters, poor soil quality, and lesser nutrient availability. More innovative technologies are immediately required to overcome these issues. In this regard, nanotechnology has contributed to the agrotechnological revolution that has imminent potential to reform the resilient agricultural system while promising food security. Therefore, nanoparticles are becoming a new-age material to transform modern agricultural practices. The variety of nanoparticle-based formulations, including nano-sized pesticides, herbicides, fungicides, fertilizers, and sensors, have been widely investigated for plant health management and soil improvement. In-depth understanding of plant and nanomaterial interactions opens new avenues toward improving crop practices through increased properties such as disease resistance, crop yield, and nutrient utilization. In this review, we highlight the critical points to address current nanotechnology-based agricultural research that could benefit productivity and food security in future.

Keywords: food, agriculture, nanotechnology, nano-pesticides, biosynthesized toxicity, bioavailability, sustainability, soil

INTRODUCTION

Agriculture acts as the primary pillar of the developing economy and provides food for a better life. In the current scenario, the field of agriculture has been facing a wide range of challenges, including unpredictable climate change, contamination of soil with various harmful environmental pollutants such as fertilizers and pesticides, and majorly elevating food demands with a growing global population (Pouratashi and Iravani, 2012). A recent report by the United Nations projected that the global population would become 8.5 billion by 2030 and approximately 9 billion by 2050 (https://population.un.org/wpp/Publications/Files/WPP2019). Therefore, to meet the demands of the relentlessly growing population, there is an urgent need to increase food production more than 50%. On the contrary, industrialization leads to depletion of natural resources on which the population's livelihood depends, such as oceans, forests, and ecological biodiversity, at an alarming rate (Kang et al., 2009). Thus, it advocates the need for increased crop production and better food security. Ecological biodiversity plays an essential role in maintaining the delicate balance of the environment and food production as it strengthens agricultural resilience toward the environmental stress that potentially leads to crop failure. More specifically, the biodiversity

for food and agriculture comprises livestock, crops, forestry, and aquaculture systems by which human beings are sustained. Oceans and forests are home to numerous animal and plant species that majorly withstand world population for food, fodder, fuel, and fiber. Thus, any issues that could cause ecological disequilibrium significantly affect food security (http://www.fao.org/3/CA3129EN/CA3129EN.pdf; https://www.un.org/sustainabledevelopment/blog/2019/05/nature-decline-unprecedented-report/; Rice and Garcia, 2011). In order to deal with these pertinent issues, newer techniques and strategies are continuously evolving. Given this, one such step taken is the introduction of nanomaterial (NM) based products for revolutionizing modern agriculture practices. These materials bear high reactivity due to their large surface area–to-volume ratio and novel physicochemical properties that provide the clear advantage of required modification according to elevating demand.

Previously, nanotechnology has been utilized in multiple fields, including chemistry, pharmaceutical science, diagnosis, and therapeutics, to name a few (Leso et al., 2019; Stefan and Monchaud, 2019; Li W. Q. et al., 2020). Nanoparticles (NPs), at the forefront of nanotechnology, are incorporated into a variety of consumer products owing to their tremendous potential as compared to their bulk counterparts (Jeevanandam et al., 2018). Therefore, the unique and emerging properties of these new-age materials have drawn unequivocal attention in the food and agriculture sector.

Modern agriculture is transforming into precision agriculture with the help of these new-age materials that are helping to gain maximum output from the available resources. Various types of other NMs, such as nanoclays, nanotubes, and nanowires, possess unique surface chemistry, electrical, and optical properties (Yaqoob et al., 2020) that provide them with better sensitivity, improved detection limits, and rapid response times (Kumbhakar et al., 2014). Fertilizers are necessary to enhance crop production, but at the other end, they decrease soil fertility by disturbing the soil mineral balance (Solanki et al., 2015). Generally, pesticides, fertilizers, and antibiotics are sprayed, which can be run off efficiently. Furthermore, the cost of production of these pesticides and fertilizers is very high, which needs to be controlled. The application of NMs in agriculture aims to reduce nutrient losses to increase yields, reduce the amounts of products for plant protection (Usman et al., 2020), and minimize the cost of production to maximize output. In the current review, we suggest and provide the facts that NMs deliver a better solution to improve agriculture and food systems. However, we also highlight the fact that it is vital to test the extent of toxicity of NM-based products before implementing them in the market. Nanotechnology-based products, such as smart agrochemical delivery systems using NMs as a carrier of active ingredients, are being continuously developed. The waste products of agriculture, such as soy hulls and wheat straw, can be converted into advanced bionanocomposites having improved mechanical and physical properties to be utilized for industrial purposes. Some progress is still needed to gain the practical advantages of nanotechnology, such as better design of processes, risk assessment of nanopesticides and nanofertilizers, and regulations

for commercialization of nanoagroproducts (Chen and Yada, 2011; de Oliveira et al., 2014; Amenta et al., 2015). Another challenging issue yet to be resolved includes farming systems to deal better with unpredictable climate variability, including new varieties of crops that can sustain drought, heat, and other environmental stress to convey the whole spectrum of modern farming practices worldwide (Elias et al., 2019). We strongly believe that a broad perspective of nanotechnology is essential to fulfilling the goal of helping foster global agriculture.

NP INTERACTION WITH PLANTS

The agricultural sector is benefiting from advancements in science and technology, which give us new ideas and solutions to combat severe problems. With the advent of nanotechnology, more efficient and fewer contaminant nanoformulations are continuously produced for sustainable agriculture (Fraceto et al., 2016). These new-age materials have the potential to alter the physiology of plants right after entering the complex plant–soil system that can be easily exploited to understand the aftereffects (**Figure 1**). Moreover, for controlled delivery of active compounds, critical knowledge of the interaction of these NMs with plants, either positive or negative, is required. Thus, they could provide novel avenues toward developing better nanomaterial-based products. It is also believed that the concentration of NMs in the natural environment is much lower than levels considered harmful. However, still, some gaps are left to be filled with comprehensive safety assessments (Batley et al., 2013).

Systemic Approach for Selectivity of NMs: Physicochemical Property-Based Uptake and Interaction

Several factors are responsible for the uptake and transformation of NPs: prominently, plant physiology, physiochemical properties of the NP itself, size, surface charge, shape, and potential interaction with plants (Pérez-de-Luque, 2017).

Size-Dependent Uptake of NPs

Size of the NPs must be considered as a significant parameter to study the uptake in plants as various barriers confined within the plants are in the range of micrometer (mm) to nanometer (nm) (**Figure 1A**). For instance, the epidermis foliar is made up of the cells that form a cuticle membrane. The epidermis consists of stomata containing two guard cells forming a pore of about 3–12 μm wide and 10–30 μm long during the opening for gaseous exchange. Therefore, NPs can make their way through the plants by virtue of these stomatal openings. Additionally, the permeation properties substantially differ for the cuticle layer on the epidermis and trichrome of the stomata. The cuticle layer, on the other hand, presents in a more significant amount on the leaf epidermis with a size exclusion limit in the nm range (Wang P. et al., 2016; Wang X. et al., 2016; **Figures 1B,C**). It was described that NPs with a size range of 4–100 nm could cross the cuticle by disrupting the waxy layer (Larue et al., 2014), and fluorescently tagged NPs >50 nm can accumulate in the epidermis underneath
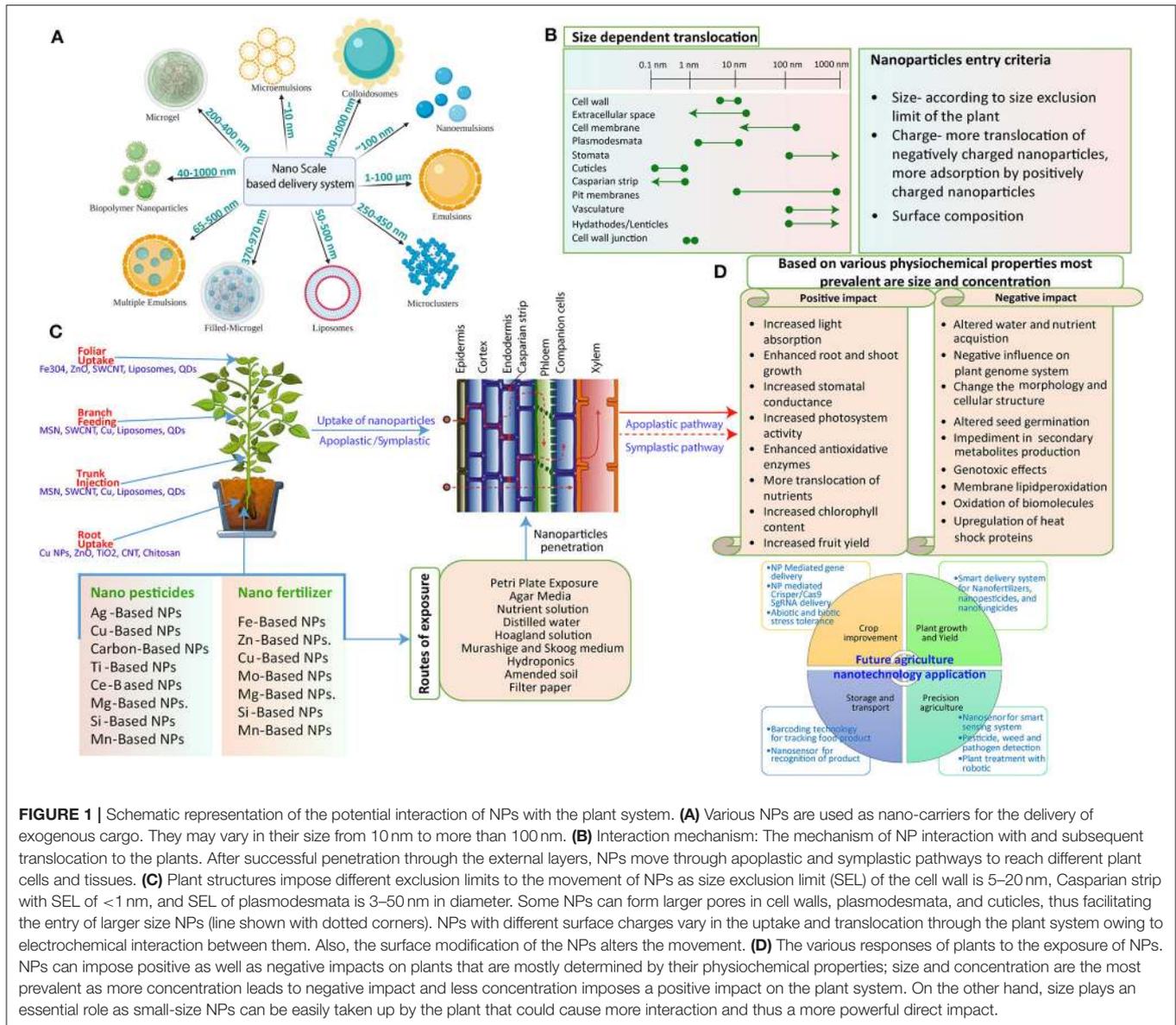
FIGURE 1 | Schematic representation of the potential interaction of NPs with the plant system. **(A)** Various NPs are used as nano-carriers for the delivery of exogenous cargo. They may vary in their size from 10 nm to more than 100 nm. **(B)** Interaction mechanism: The mechanism of NP interaction with and subsequent translocation to the plants. After successful penetration through the external layers, NPs move through apoplastic and symplastic pathways to reach different plant cells and tissues. **(C)** Plant structures impose different exclusion limits to the movement of NPs as size exclusion limit (SEL) of the cell wall is 5–20 nm, Casparian strip with SEL of <1 nm, and SEL of plasmodesmata is 3–50 nm in diameter. Some NPs can form larger pores in cell walls, plasmodesmata, and cuticles, thus facilitating the entry of larger size NPs (line shown with dotted corners). NPs with different surface charges vary in the uptake and translocation through the plant system owing to electrochemical interaction between them. Also, the surface modification of the NPs alters the movement. **(D)** The various responses of plants to the exposure of NPs. NPs can impose positive as well as negative impacts on plants that are mostly determined by their physiochemical properties; size and concentration are the most prevalent as more concentration leads to negative impact and less concentration imposes a positive impact on the plant system. On the other hand, size plays an essential role as small-size NPs can be easily taken up by the plant that could cause more interaction and thus a more powerful direct impact.

the cuticle where stomata are absent (Nadiminti et al., 2013). The polymeric NPs of 43 nm diameter are able to penetrate the leaves of *Vicia faba* solely through the stomata, whereas particles of 1 μm did not cross at all (Eichert et al., 2008). NPs usually get deposited on the cell wall of the substomatal cavity when entering through the stomata. The likely penetration of small-size NPs, for instance, 20 nm Fe_3O_4 NPs, were observed through TEM studies in the *Nicotiana benthamiana* plant (Cai et al., 2020; **Figures 1B,C**).

The principal size exclusion limit was mainly imposed (Palocci et al., 2017), notably, by these plant cell walls that are usually in the size range of 3.5–20 nm and more often around 5 nm (Carpita et al., 1979; Tepfer and Taylor, 1981). Thus, NPs smaller than 5 nm can traverse the cell wall of intact cells efficiently. In one study, SWCNT was able to form an endocytosis-like structure in

the intact cell wall of the *Arabidopsis thaliana* plant (Shen et al., 2010). It is suggested that NPs within a size range limit according to the cell wall can traverse through it. For example, quantum dots (QDs) fall under the size range of plant cell wall pores (sub-10 nm) that can be easily exploited to make their entry through the plants (Wu et al., 2017a). Li et al. observed the presence of AgNPs of size 24.8–38.6 nm within lettuce leaves when applied through the foliar route. They also demonstrated the in planta transformation of $AgNO_3$ applied with AgNPs that also explains the biotransformation phenomenon (Li W. Q. et al., 2020).

The interaction of NPs with the cell wall creates large-size pores that further facilitate the entry of NPs (Carlson et al., 2008). Further, there are results on the accumulation of larger sized NPs in the cell wall and subsequently in the cytoplasm, but a discrepancy between the claimed pore size of the cell wall

(depends on many factors) and the accumulation of larger sized NPs is still maintained. Several studies carried on plant protoplast utilized as a model system to study NP uptake through the plant cell membrane. Moreover, this circumvents the technical difficulties arise in studying uptake as well as quantification of NPs inside the plants mostly due to the internal fluorescence of the plant cell wall and impermeability imposed by plants to certain staining dyes (Torney et al., 2007).

After NP entry into the plants, it is imperative to recognize the path that they follow to transport as it gives an idea of where these NPs might accumulate. NPs follow two important routes for moving up and down in a plant: the apoplast and the symplast. The symplastic pathway allows movement through the cytoplasm of adjacent cells (Roberts and Oparka, 2003), whereas the apoplastic pathway allows flow through the extracellular spaces involving cell walls of neighboring cells and xylem vessels (Sattelmacher, 2001). The cell-to-cell movement takes place through the passage plasmodesmata, serving as a cytoplasmic bridge to facilitate particle movement between neighboring cells. They are about 20–50 nm in diameter, surrounded by 3-nm particles (Dietz and Herth, 2011).

Surface Charge-Dependent Uptake of NPs

NPs have a great degree of freedom that essentially relies on their uptake, absorption, and trafficking inside plants. The physicochemical interaction of NMs with plants under their energy and surface charge results in modifying the surface receptors, transporters, and specific membrane proteins (Juárez-Maldonado et al., 2019). NPs with different surface charge possess the differential capacity for aggregation and surface properties in comparison to their pristine counterparts (Hotze et al., 2010; **Figure 1C**).

Inside the leaves, a biological membrane, i.e., the cell wall, is present with both hydrophobic and hydrophilic components and unequal distribution of fixed negative charges (surface potential of cellulose fibers and lignin are −15 and −45 mV, respectively) (Santiago et al., 2013; Zeng et al., 2017). Thus, a possible explanation lies in that the negatively charged cell wall favors the uptake of positively charged NPs in the tissues. The negatively charged plant cell walls act as the surface for the ion exchange that potentially promotes the penetration of cationic rather than anionic NPs (Meychik et al., 2005). In contrast to this, transport efficiency is greatly enhanced for negatively charged NPs. The surface charge–dependent uptake and transportation of AuNPs is explained by Zhu et al., who show much higher adsorption of positively charged NPs at root surfaces. However, negatively charged NPs were observed to have a higher internalization rate and translocation (Zhu et al., 2012). In this context, CeO NPs with a positive charge strongly adsorbed onto the root surfaces (negatively charged), whereas negatively charged CeO_2 NPs showed low root accumulation but higher shoot internalization, mainly by overcoming electrostatic repulsion (Liu et al., 2019; **Figure 1D**).

Similarly, Milewska-Hendel et al. comprehensively demonstrate the surface charge–dependent uptake of AuNPs in roots and its transportation from roots to shoots (Milewska-Hendel et al., 2019). It is thought that negatively charged NPs

assist both symplastic as well as apoplastic transport into the vascular system through roots to shoots. Thus, the transport performance of the NPs across plants is significantly varied through surface charge modification (**Figures 1B,C**). Based on the physicochemical properties and concentration of NPs in conjunction with agrochemicals exert positive as well as negative impact on plant health (**Figure 1D**). The review contains comprehensive information on various impacts, and the future prospect of NPs in agriculture is discussed.
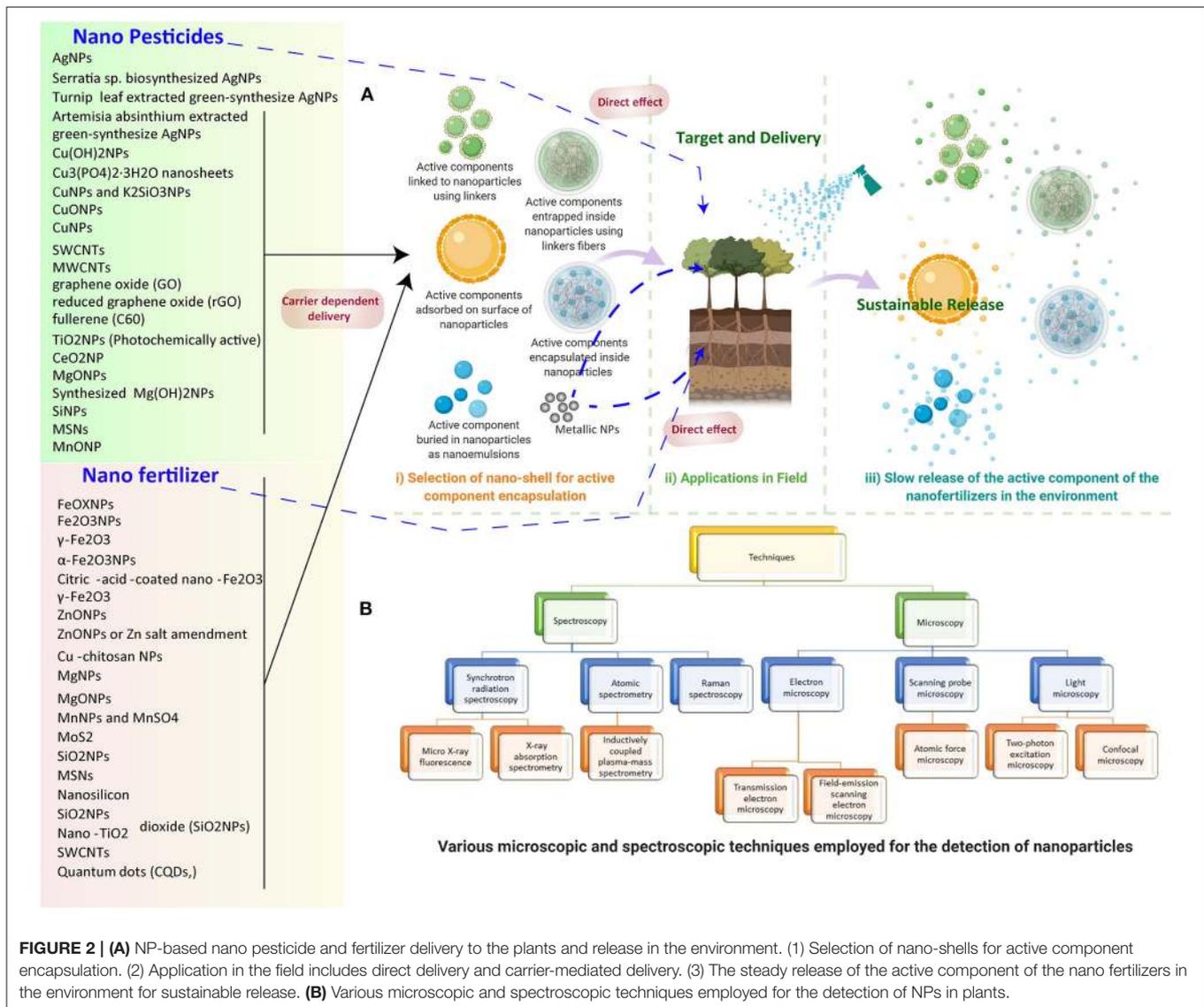
Anatomical Difference and Mode of Application-Related NP Uptake

The anatomical differences in a plant and the surface charge of the NPs are very closely related. A better association of positively charged cerium oxide NPs is found with dicot plants, such as tomato and lettuce, with a larger root surface area. However, better root-to-shoot translocation is observed with neutral and negatively charged NPs (Spielman-Sun et al., 2019). This suggests that anatomical and physiological differences in plants result in differential uptake patterns of NMs, which is also evidenced by observations that diverse crops belonging to different species show a varied pattern of accumulation and absorption of distinct classes (e.g., TiO_2, carbon-coated, Au) of NMs (Cifuentes et al., 2010; Larue et al., 2012c; **Figures 1B**, **2A**).

The dicots, in comparison to monocot plants, show higher uptake of NPs due to more permeability in the cuticles. This is proven in the case of lipid-based liquid crystalline nanostructures, which are utilized as a delivery vehicle (Nadiminti et al., 2013). This difference is attributed to the different architecture of the cell wall in monocots and dicots. In monocots, the pectin polymer is less tightly bound to the cellulose (Carpita and Gibeaut, 1993). Another significant anatomical difference is in the leaf architecture, such as the presence of dumbbell-shaped stomata in monocot and kidney-shaped stomata in dicot plants, resulting in variable degrees of uptake and translocation efficiencies of NPs (**Figures 1B**, **2A**).

Additionally, the leaves of monocots have parallel veins that are most resistant to tearing and, therefore, have high strength (Avellan et al., 2017; Hu et al., 2020). The ability of plants to take up these NMs also depends upon the mode of their application as roots absorb nutrients from the soil, leaves are meant for the exchange of gas, and cuticles hamper the penetration of any substance freely (Schwab et al., 2016). However, drought-resistant plants develop tighter cell walls, cuticles, Casparian strips, and other barriers that are helpful to minimize water loss during scarce water conditions (Riederer and Schreiber, 2001). Some of the essential factors of the soil, such as organic matter and humic acid, make NMs more stable, which, conversely, enhances their bioavailability (Navarro et al., 2012). The presence of bacteria and mycorrhizal fungi living in association with plants also affects the plant uptake of NPs (Feng et al., 2013). The transport of CuO NPs from root to shoot and its reverse transport from shoots back to roots takes place via xylem and phloem, respectively (Wang Z. et al., 2012).

NPs can also utilize a clathrin-independent endocytic pathway for gaining entry into the plant. Poly (lactic-co-glycolic) acid (PLGA) NPs follow this pathway as treatment of inhibitors

FIGURE 2 | (A) NP-based nano pesticide and fertilizer delivery to the plants and release in the environment. (1) Selection of nano-shells for active component encapsulation. (2) Application in the field includes direct delivery and carrier-mediated delivery. (3) The steady release of the active component of the nano fertilizers in the environment for sustainable release. **(B)** Various microscopic and spectroscopic techniques employed for the detection of NPs in plants.

of the clathrin-dependent pathway do not hamper its uptake into the grapevine (*V. vinifera*) protoplast. The size and surface characteristics of the NPs play essential roles in determining the uptake inside the plants as evidenced by a study conducted on foliar uptake of AuNPs on wheat that explains efficient translocation of smaller size NPs with a surface coating of PVP-AuNPs rather than citrate-AuNPs (Avellan et al., 2019). Another study shows no uptake of SWCNT by cucumber seedlings, but in the form of nanosheets, they were able to interact with the external surface of the roots (Cañas et al., 2008). It shows that the uptake of NMs is highly dependent on the type of delivery method used. In this context, Su et al. investigated the fate and mobility of surface-modified AgNP delivery to trees by employing various methods, including direct tree injection and petiole feeding in Mexican lime citrus trees (Su et al., 2020). Further explanation of uptake and transport in conjunction with the fate and transformation of NMs is comprehensively reviewed by different groups (Lv et al., 2019; Su et al., 2019).

Methods to Study Uptake, Quantification, and Translocation of NPs

Potential techniques must be developed to track the interaction taking place between plants and NMs; moreover, more vital information is needed to quantify the uptake and translocation of NPs inside plants and as released in the environment (**Figure 2A**). In this context, the assimilation and concentration of iron (Fe_3O_4) NPs in pumpkin (*Cucurbita maxima*) plants were quantified by employing a vibrating sample magnetometer to confirm the presence in roots and leaves (Zhu et al., 2008). Similarly, Fe_3O_4 NPs can also be measured and tracked in plant organs by exploiting its magnetic properties, such as temperature and magnetic field dependence of magnetization (Govea-Alcaide et al., 2016). The major problem with tracking and translocation of Fe_3O_4 NPs is associated with the inability to distinguish between intact Fe_3O_4 NPs and leached ions, which further can be solved by utilizing magnetic particle spectrometry in conjunction with

conventional atomic absorption spectroscopy (Ju et al., 2019; **Figure 2B**).

Also, the electron microscopy technique was used to track the translocation of C_{70} fullerene and MWCNT from roots to aerial parts (leaves) of rice (*Oryza sativa*); however, the authors did not quantify the amount of NPs taken up by the plants (Lin et al., 2009). In this regard, the uptake of MWCNTs in wheat and rapeseed plants was quantified through transmission electron microscopy (TEM) and the Raman spectroscopy technique (Larue et al., 2012b).

Critical imaging techniques, such as X-ray and computed tomography (CT), are beneficial to detect and localize various NMs in plants. Recently, to localize gold NPs in the roots of *A. thaliana,* a combination of techniques such as X-ray computed nanotomography (nano-CT), enhanced dark field, and hyperspectral (DF-HSI) imaging was used. The combined use of 2-D (DF-HSI) and 3-D (nano-CT) techniques provides better means to characterize and evaluate the NP–plant interaction at the cellular level (Avellan et al., 2017). Another non-invasive, highly sensitive method to visualize NPs through the combination of autoradiography, positron emission tomography (PET)/CT, TEM, and SEM was demonstrated in lettuce (*Lactuca sativa*) (Davis et al., 2017). In a pioneering study, the effect and interaction of TiO$_2$ NPs with garlic (*Allium sativum*) was observed through spectroscopic techniques using time-resolved, laser-induced fluorescence and ultraviolet-visible spectra. The resulting increased chlorophyll content and enhanced photosynthetic activity in leaves of garlic plants were observed as compared to the control. The authors reported a decrease in the intensity ratio of red and far red chlorophyll fluorescence bands, suggesting a rise in photosynthetic activity and chlorophyll content (Bharti et al., 2018). Two-photon excitation microscopy as a novel strategy was employed for *in vivo* detection of MWCNTs, TiO$_2$, and Cerium oxide NPs in wheat tissues (Wild and Jones, 2009). Other essential techniques, such as microscopy and spectroscopy, are highlighted in **Figure 2B**.

Although microscopy techniques provide a clear advantage in analyzing NPs in different samples, they have some main limitations, including sample preparation, a partial area of analysis, and limited 3-D imaging, which further requires alternative solutions. In view of this, inductively coupled plasma-mass spectroscopy (ICP-MS), in particular, single-particle ICP-MS (SP-ICP-MS) analysis, is a promising method for detection, characterization, and quantification of NMs (Mozhayeva and Engelhard, 2020). Similarly, SP-ICP-MS is utilized to quantify the uptake of CuO NPs in edible plants, lettuce, kale, and collard greens (Keller et al., 2018).

Mass spectrometry–based analytical techniques help distinguish between different chemical forms of NMs as they can readily be transformed once they enter the plant. One such approach utilized SP-ICP-MS and ESI tandem MS to confirm the fate of ZnO NPs inside the edible plant lettuce (Wojcieszek et al., 2019). The Au NPs were quantified by using ICP-MS in order to observe the uptake mode and accumulation in watermelon plants (Raliya et al., 2016). The significant advantage of these potential techniques lies in either their cumulative power or utilizing

them in combination. The simultaneous uptake, retention, and distribution along with the plant were studied by Nath et al. for Ag, Cu, and ZnO NPs in *A. thaliana* using SP-ICP-MS, SEM, and EDS (Nath et al., 2018). Similarly, the combination of three orthogonal techniques, such as electron microscopy, SP-ICP-MS, and ICP-OES, is used to study the uptake and size distribution of TiO$_2$ NPs in rice plant (*Oryza sativa* L.) tissues (Deng et al., 2017).

The Physiochemical Response of Plants Toward NPs

NPs for Plant Growth and Seed Germination

The uptake of NMs inside plants largely depends on the size, chemical composition, and functional groups present on their surface and the type of coating. The interaction and uptake of NMs lead to changes at the molecular level and affect the overall physiology of plants (Jin et al., 2017). The promising effect of multiwalled carbon nanotubes (MWCNTs) on the growth (55–64% increase) of tobacco cells involves a unique molecular mechanism. The majority of the activated genes involved are related to cell division (CycB), cell wall extension (NtLRX1), and tobacco aquaporin (NtPIP1) (Khodakovskaya et al., 2012). The ability of NMs to penetrate the hard coating of seeds and allow water importation is the deciding factor for increased growth and vigor. In addition to this, the seed priming technique with the help of nanotechnology is a promising strategy; before sowing, it further corroborates the potential of high-yield value crops (Acharya et al., 2020; Anand et al., 2020).

The application of MWCNTs affects the growth of some important crops, such as barley, soybeans, and corn. MWCNTs aggregate inside the endosperm of exposed seeds, which was confirmed by Raman spectroscopy and TEM imaging (Lahiani et al., 2013). NPs were transported to different parts of the plant and interacted with cellular machinery, thus promoting plant growth. NPs made of mesoporous silica (MSNs) can improve photosynthesis by interacting with chloroplasts, resulting in enhanced seed germination, increased total protein, and chlorophyll content. The highest concentration (2,000 mg/l) of MSNs did not induce stress conditions in any of the plants, which is indicative of its safer application as a smart delivery system (Sun et al., 2016). Silica plays an essential role in providing nutrition as its deficiency consequently makes plants weaker and highly susceptible to biotic and abiotic stress (Rafi et al., 1997). The application of silica also helps to ameliorate the effect of drought stress and increase biomass in stress-affected plants (Ahmad et al., 2007). Maize plants show better response toward the application of silica NPs (SiO$_2$ NPs) prepared from rice husk and thoroughly characterized as compared to its bulk counterpart and control. Silica uptake was enhanced, and roots were elongated in the maize plants; this helps to withstand drought conditions. Root sectioning also reveals the direct uptake and accumulation of SiO$_2$ NPs in the epidermis cells of maize (Suriyaprabha et al., 2012). The detailed impact of SiO$_2$ NPs on agriculture has been extensively reviewed by Rastogi et al. (2019).

Another potential NP such as TiO$_2$ also promotes the growth of plants as evidenced in canola (*Brassica napus*), which resulted

in promoted seed germination as well as seed vigor. The highest effect was seen at a concentration range of 1,200–1,500 mg/l with increased plumule growth and large radicle as compared to the control (Mahmoodzadeh et al., 2013). The effect of any NP can be positive and negative, depending on its additive concentration and size. The smallest TiO_2 NPs accumulate more in plants as compared to larger particles (Larue et al., 2012a). Moreover, these NPs can also affect the miRNA levels to initiate the growth-promoting pathways in plants (Boykov et al., 2019).

The positive effect of Fe NPs on the *Capsicum annum* plant at lower concentrations was found with increased plant growth by increasing chloroplast number and grana stacking. In contrast, when these NPs were applied at higher levels, they caused harm to the plant (Yuan et al., 2018). Other metal oxide NPs, such as ZnO and Cu, are observed to affect seed germination in *Vigna mungo,* i.e., black gram (Raja et al., 2019). The seed germination and growth-enhancing properties of less studied polyvinylpyrrolidone (PVP) protected platinum NPs in *Pisum sativum* (Rahman et al., 2020). Another critical and biocompatible NP, chitosan, exerted its effect on seed germination and growth by elevating the levels of indole-3-acetic acid (IAA) concentration in wheat or *Triticum aestivum* L. even at a shallow concentration (Li et al., 2019).

RECENT ADVANCES IN NPs FOR PLANT PROTECTION

The application of NPs (described in the previous sections) influence various important factors of the plant's growth and development that include photosynthesis, seedling vigor, and growth of roots and shoots. Plants are found everywhere; therefore, they have to bear extreme environmental conditions, such as drought, salt stress, high temperature, UV radiation, and salt stress. A number of different stress responses is shown by plants, such as alterations in molecular mechanisms, stress-responsive gene expression, and production of antioxidative enzymes that help to play a central role in scavenging the plants in harsh environmental conditions (Rejeb et al., 2014). Plants protect themselves from osmotic stress by producing various organic osmolytes, such as polyols and trehalose, and also different amino acids, such as proline and glycine. NPs provide an efficient way or, in other words, provide support to plants in alleviating this protection mechanism.

NPs Mitigate Abiotic Stress Response
In addition to helping plants grow, NPs also protect them from abiotic stress. Toxic metal binds to the surface of the NP owing to its large surface area and small size, thus reducing its availability. Abiotic stress includes drought, salinity, alkalinity, temperature fluctuations, and mineral and metal toxicity. NPs can mimic the activity of antioxidant enzymes in the form of nano-enzymes that can scavenge from oxidative stress (Sharifi et al., 2020). Photosynthesis is the vital metabolic process in plants and one of the highly susceptible methods; thus, by mitigating oxidative and osmotic stress, its normal functioning can be maintained. In the photosynthetic machinery, photosystem II (PS II), Rubisco, and
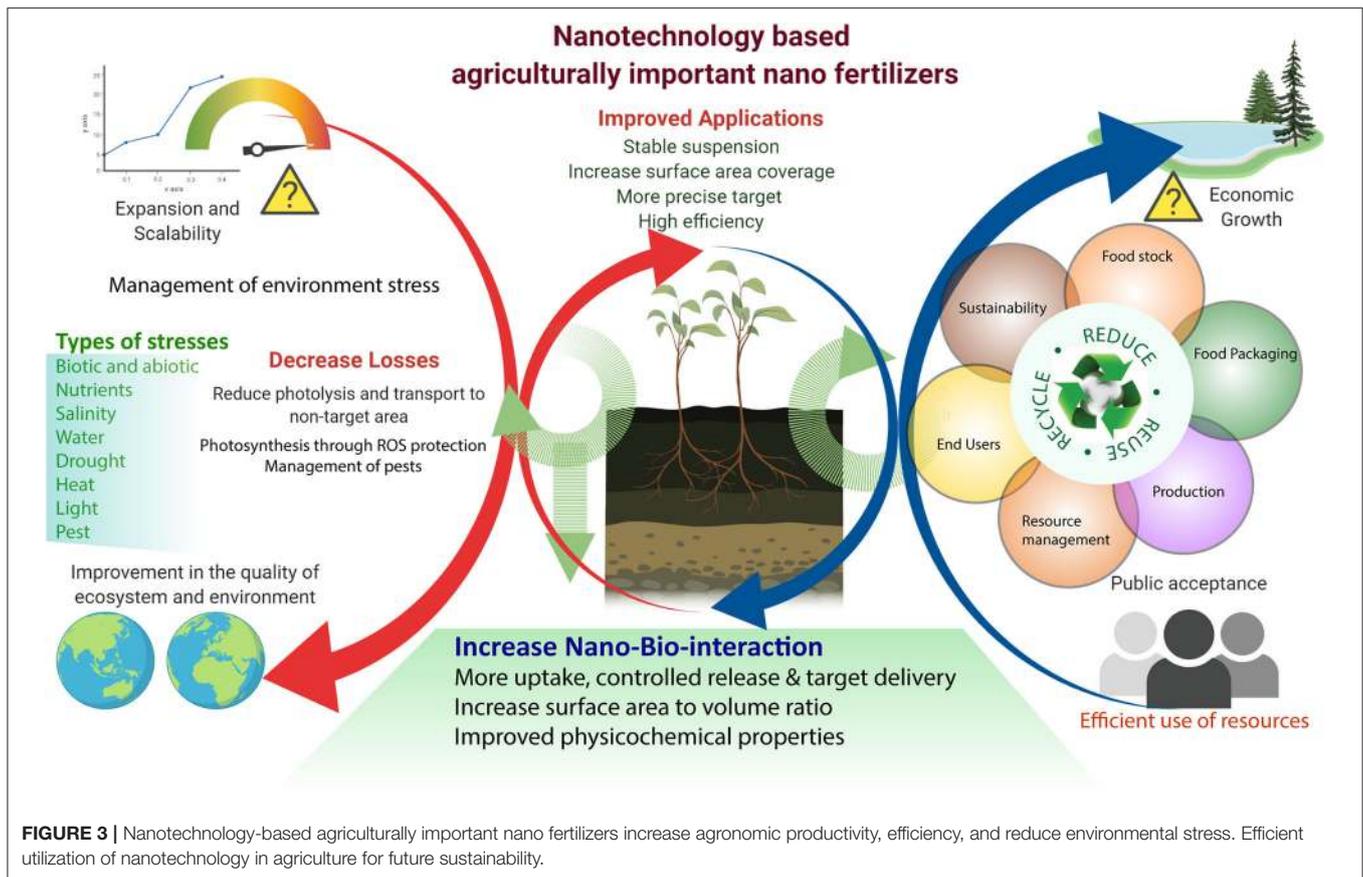
ATP are the primary targets under stress conditions (e.g., nutrient deficiency, salinity, water, drought, and heat; **Figure 3**).

Th defense response in plants against abiotic stress was studied; for example, SiO_2 NPs improved plant transpiration rate, water use efficiency, total chlorophyll, and carbonic anhydrase activity in the *Cucurbita pepo* plant in response to a defense mechanism against salt stress (Siddiqui et al., 2014). Similarly, it was found that TiO_2 (anatase) changes the photoreduction activity and inhibits linolenic acid in the electron transport chain. It also decreased the rate of oxygen evolution of chloroplasts (Mingyu et al., 2008). In stress conditions, ROS are produced by the cell organelles, and this is the signature of abiotic stress. Plants are also equipped with the enzymatic machinery to deal with the oxidative stress imposed by the environment on them (**Figure 3**). However, plants face the consequences of such a situation when stress overcomes the defense system. NMs help in mitigating such stress by activating specific genes, accumulating osmolytes, and providing free nutrients and amino acids (**Table 1**).

Cerium NPs (CeO NPs)
Nanoceria has broad implications on plant health, both positive and negative, depending on the exposure concentration, coating, surface charge, plant species, and growth conditions (Milenković et al., 2019). Nanoceria is a family of CeO NPs with wide application as an antioxidant in the biomedical industry (Liu and Shi, 2019). Although NPs can impose some severe effects on plants, as we look into the positive aspects of these NPs, it outweighs the negative impacts and can be exploited to provide health benefits to plants (**Table 1**). As we discuss earlier, the potential interaction at the nano–bio interface, these NPs could augment the tolerance against various abiotic stress of plants by regulating essential pathways (Saxena et al., 2016). For instance, abiotic stress leads to excessive ROS production that consequently decreases the photosynthetic performance of the plant and could cause biomolecule oxidation (Wakeel et al., 2020). Thus nano-Ce is well-suitable to mitigate this effect owing to the unique redox potential based on the facile transition between Ce^{3+} and Ce^{4+} oxidation states (Collin et al., 2014) and, therefore, acts as an ROS scavenger.

Moreover, a CeO NP with its high Ce^{3+}/Ce^{4+} ratio mimics superoxide dismutase and produces hydrogen peroxide, but it also mimics catalase activity at a low Ce^{3+}/Ce^{4+} ratio and shows the scavenging effect (Wang Q. et al., 2012; Wang Z. et al., 2012; Ma et al., 2015; Pulido-Reyes et al., 2015). In addition, the oxidative scavenging effect also is extended to other stresses, which include excess light, heat, and dark chilling. Furthermore, it leads to decrease photosystem II abundance, photochemical efficiency, chlorophyll content, and changed plant morphology (Nievola et al., 2017; Chen et al., 2020; Gao et al., 2020). Wu et al. explained the ameliorative effect of the anionic CeO NPs in the *A. thaliana* plant against abiotic stress, including excess heat, light, dark, and chilling (Wu et al., 2017b). The salinity stress also imposes a threat to plant physiology by a similar mechanism of oxidative stress. It was found that CeO NPs could alleviate the oxidative stress in *Brassica napus*. The effect was imposed by NaCl (100 mM) by modifying physiobiochemical properties, such as increased plant biomass, chlorophyll content (which, in

FIGURE 3 | Nanotechnology-based agriculturally important nano fertilizers increase agronomic productivity, efficiency, and reduce environmental stress. Efficient utilization of nanotechnology in agriculture for future sustainability.

turn, increases the Mg^{2+} uptake), and efficient photosystem at a concentration of 200 and 1,000 mg/kg (Rossi et al., 2016).

The maintenance of the cytosolic Na^+/K^+ ratio is considered one of the hallmarks of salinity stress (Hauser and Horie, 2010), and NPs can affect this transport efficiently. Wu et al. demonstrated that nanoceria could augment plant tolerance to salinity stress. By directly acting on hydroxyl radical ($\cdot OH$) generation and affecting potassium fluxes (reducing K^+ efflux and improving K^+ retention) across the plasma membrane of mesophyll thus improves plant photosynthetic performance and biomass (Wu et al., 2018). The catalytic scavenging activity of CeO NPs has also been utilized to mitigate drought stress, which, in particular, has severe implications for plant growth and yield worldwide. The highly efficient, drought-resistance activity of CeO NPs was observed in foliar-sprayed sorghum plants at a shallow concentration of 10 mg/L.

Additionally, it alleviated the ROS percentage and lipid peroxidation, resulting in improved carbon assimilation rates as well as pollen germination associated with it (Djanaguiraman et al., 2018b). Seedling stage effects of salinity stress could be mitigated by CeO NPs. Seeds primed with poly (acrylic acid)-coated CeO NPs (500 mg/L in water for 24 h) when germinated in salinity stress (200 mM NaCl) showed drastic effects on the seedling roots, including increased length (56%), weight (41%), and root vitality (114%) as compared to the control. The subsequent perturbation of pathways related to the antioxidative

enzyme system, ion binding and Ca^{2+} signaling, and terpene synthesis result in mitigation of oxidative stress and enhanced tolerance against salinity stress (An et al., 2020).

Silicon NPs (SiNPs)

Silicon (Si) is known to be the second most abundant material on Earth after oxygen, and it has gained significant importance in agriculture (**Table 1**). Si is considered to be midway between an essential and non-essential element for plants because it is not merely responsible for plant survival, but if present, plants can sufficiently benefit (Luyckx et al., 2017). These NPs can directly or indirectly interact with plants, thus conferring morphological and physiological changes in order to provide tolerance against stress. It confers beneficial effects on plant growth; increases their biomass, anatomy, and physiology; modifies tissue differentiation; activates defense systems; and helps in acclimatizing to stress conditions (Babajani et al., 2019).

SiNPs showed anti-stress effects at various concentrations toward drought stress in Hawthorns (*Crataegus* sp.); the responses varied in the seedlings depending on the concentration applied at different stages of drought stress, i.e., moderate to severe. These effects include enhanced photosynthetic ability; relative water content; membrane electrolyte leakage; and increased levels of chlorophylls, carotenoids, and proline (Ashkavand et al., 2015). The increased tolerance under a

TABLE 1 | Types of NPs, their relevant sizes, and concentration with the application focus and effect found on alleviating abiotic stress response in plants.

S.No	NPs	Size (nm)	Concentration	Plant species	Application	Effect	Type of stress	References
1	TiO_2	10–25 nm	0, 10, 100, and 500 mg/L	*Linum usitatissimum*	Leaf treatment	Increased carotenoids and chlorophyll content, decreased MDA activity and levels of H_2O_2	Drought	Aghdam et al., 2016
2	TiO_2	NA	0.01, 0.02, and 0.03%	*Triticum aestivum* L. c.v "Pishtaz"	Spraying by backpack sprayer	Starch content increased, enhanced growth, yield, and gluten	Drought	Jaberzadeh et al., 2013
3	TiO_2	7–40 nm	0, 2, 5, and 10 ppm	*Cicer arietinum* L.	Amended soil	Deceased electrolyte leakage index and MDA levels	Cold stress	Mohammadi et al., 2013
4	TiO_2	10–25 nm	500, 1,000, and 2,000 mg/kg	*Triticum aestivum*	Amended soil	Enhanced seedling dry weight, relative water content, antioxidative enzymes, increased total chlorophyll and carotenoids, improved stomatal conductance, and transpiration rate	Drought stress	Faraji and Sepehri, 2020
5	ZnO	NA	0, 0.5, and 1 g/L	*Glycine max*	Petri dish exposure	Rate of germination and percentage increased but decreased dry weight	Drought	Sedghi et al., 2013
6	ZnO	16–35 nm	10 mg/L	*Abelmoschus esculentus* L. Moench	Foliar application	Increased photosynthetic pigments, activity of SOD and CAT, reduced proline, and total soluble sugar contents	Salinity stress	Alabdallah and Alzahrani, 2020
7	ZnO and Si	ZnO <100 nm, SiNP 5–15 nm	50, 100, 150 mg/L; ZnO NPs and 150, 300 mg/L; SiNPs	*Mangifera indica* L.	Foliar spray	Improved plant growth, nutrients uptake, and carbon assimilation	Salinity stress	Elsheery et al., 2020
8	Yttrium doped Fe_2O_3	1–10 nm	100, 160, 200, and 400 mg per plant	*Brassica napus*	Nutrient solution	Reduced levels of hydrogen peroxide and MDA, enhanced leaf growth rates, and chlorophyll content	Drought	Palmqvist et al., 2017
9	SiO_2	20 nm	0.5, 1, 2, and 3 mM	*Solanum lycopersicum* L.	Exposure *in vitro*	Salt stress genes were up and downregulated significantly help to mitigate the salt stress	Salinity stress	Almutairi, 2016
10	SiO_2	10–20 nm	50 and 100 mg/L	Strawberry	Exposure in nutrient sol	Improved vegetative growth, increased proline, chlorophyll, improved epicuticular wax layer, leaf relative water content, improved canopy temperature	Salnity stress	Avestan et al., 2019
11	SiO_2	NA	0, 200, 400, and 600 mg/L	*Musa acuminata* "Grand Nain"	*In vitro*	Enhanced shoot growth and chlorophyll content, improved photosynthesis, maintains K^+ and Na^+ balance, decreases cell wall damage	Salinity and water deficit	Mahmoud et al., 2020
12	Fe_2O_3	27.3–34.62 nm	0, 10, 20, and 30 μM	*Mentha piperita* L.	Hoagland solution	Reduced proline and MDA levels, the suppressed activity of antioxidative enzymes	Salinity	Askary et al., 2017
13	Fe_3O_4	40–53 nm	0.8 ppm	*Fragaria×ananassa* Duch	Murashige and Skoog medium	Enhanced plantlets growth parameters	Drought stress	Mozafari et al., 2018
14	$FeSO_4$	99 nm	2 g/L	*Helianthus annuus* L. cvs. Alstar, Olsion, Yourflor, Hysun36, and Hysun33	Foliar spray	Increased leaf area, shoot dry weight, net carbon dioxide (CO_2) assimilation rate (A), sub-stomatal CO_2 concentration (Ci), chlorophyll content, Fv/Fm and iron (Fe) content, and decreased sodium (Na) content	Salinity stress	Torabian et al., 2017
15	Fe_3O_3	20–40 nm	0, 30, 60, and 90 ppm	*Dracocephalum moldavica* L.	Foliar application	Increased the leaf area, phenolic, flavonoid and anthocyanin content and the activity of guaiacol peroxidase, ascorbate peroxidase, catalase, and glutathione reductase enzymes were enhanced	Salinity stress	Moradbeygi et al., 2020
16	FeNPs	50–100 nm	0, 25, 50, and 100 mg/kg	*Triticum aestivum*	Potting soil	Improved growth and physiology, enhanced photosynthesis, Fe concentration, and reduced cadmium concentration	Cadmium and drought stress	Adrees et al., 2020

(Continued)

TABLE 1 | Continued

S.No	NPs	Size (nm)	Concentration	Plant species	Application	Effect	Type of stress	References
17	AgNPs	34 nm	25, 50, and 75, 100 mg/L	*Triticum aestivum*	Potting soil	Improved root and shoot length, root number, increased morphological growth of the plant-like increased leaf area, and number	Heat stress	Iqbal et al., 2019
18	AgNPs	15–29 nm	0, 2, 5, and 10 mM	*Triticum aestivum*	Seed priming	Decreased antioxidative enzyme activity, increased POD activity, proline, sugar content	Salinity stress	Mohamed et al., 2017
19	AgNPs	NA	0, 10, 20, 30, and 40 µg mL^{-1}	*Trigonella foenum-graecum*	Petri dish exposure	Enhanced germination rate, improved fresh, and dry mass	Salinity stress	Hojjat and Kamyab, 2017
20	AgNPs	15–30 nm	1 mg/L	*Triticum aestivum*	Seed priming	Wheat germination, growth, induce synthesis of IBA, NAA, BAP contents, and reduced ABA	Salinity stress	Abou-Zeid and Ismail, 2018
21	Al$_2$O$_3$	5, 30–60, and 135 nm	50 ppm	*Glycine max* L. cv. Enrei	Petri dish exposure	Increased hycotyle length, glycolysis related protein synthesis, increased mitochondrial membrane protein	Flooding stress	Mustafa and Komatsu, 2016
22	Chitosan-PVA and CuNPs	95 nm	50, 100, and 150 mg/L	*Solanum lycopersicum* L.	Nutrient solution	Increased growth chlorophyll a b content, carotenoids, SOD, Vitamin C and lycopene	Saline stress	Hernández-Hernández et al., 2018
23	CuNPs	30–40 nm	3.333, 4.444, and 5.556 mg/L	*Zea mays*	Plants priming	Higher leaf water content and plant biomass, increased anthocyanin, chlorophyll and carotenoid contents, increased total seed number, and grain yield	Drought stress	Van Ha et al., 2020
24	SeNPs	10–40 nm	10 mg/L	*Sorghum bicolor* (L.) Moench	Foliar and water spray	Improved antioxidant system, improved thylakoid membrane integrity, and composition	Heat stress	Djanaguiraman et al., 2018a
25	SeNPs	8–15 nm	0, 1, 4, 8, and 12 µM	*Lycopersicum esculentum* Mill. cv. "Halil"	Hydroponic solution	Improved shoot fresh, dry weight and diameter, root fresh and dry weight and root volume	Low and high temperature stress	Haghighi et al., 2014
26	SiNPs	10–95 nm	10 µM	*Triticum aestivum*	Nutrient solution	Enhanced antioxidants to protect against UV-B generated oxidative stress	UV-B stress	Tripathi et al., 2017
27	MnNPs	NA	0.1, 0.5, and 1 mg/L	*Capsicum annuum* L.	Nanopriming	Implies the role in plant salt stress management in order to promote sustainable agriculture	Salinity stress	Ye et al., 2020
28	Poly(acrylic)-CeO NPs	10.3 nm	∼50 mg/L	*Arabidopsis thaliana*	Leaf infiltration	Increased quantum yield of photosystem II, carbon assimilation rates and rubisco carboxylation rates to scavenge photosynthesis and ROS	Multiple stress	Wu et al., 2017a
29	CeO NPs	2.1 ± 1.4 nm	500 mg/L	*Gossypium hirsutum* L.	Seed priming	Decreased ROS levels, improved root parameters, trigger tolerance pathways including ion homeostasis	Salinity stress	An et al., 2020
30	MWCNT	Diameter:5–15 nm Length: ∼50 µm	10, 30, 50, 100, and 200 mg/L	*Dodonaeaviscosa* L.	Nano priming	Improved seed germination percentage, mean germination time, root and stem lengths, fresh and dry weights of root and stem	Drought stress	Yousefi et al., 2017
31	CNTs and graphene	13–18 nm	50 and 200 µg/ml	*Catharanthus roseus*	Murashige and Skoog medium	Increased the total number of flowers and leaves	Salinity stress	McGehee et al., 2019
32	CNTs and graphene	13–18 nm	50 and 200 µg/ml	*Gossypium hirsutum*	Seed priming	Increased fiber biomass, increased root and shoot growth of young seedlings	Drought stress	Pandey et al., 2019
33	Chitosan NPs	10–20 µm	0, 30, 60, and 90 ppm	*Hordeum vulgare* L.	Foliar application	Increased the relative water content, the grain weight, the grain protein, the proline content, the CAT and SOD	Drought stress	Behboudi et al., 2018

NA, not available.

saline environment conferred by the application of Nano-SiO$_2$ by accumulating proline maintained the ionic balance, enhanced the antioxidant system, and increased levels of various phytopropanoids, thus leading to osmotic adjustments (Soleymanzadeh et al., 2020). Additionally, under salt stress, SiO$_2$ NPs are shown to increase water use efficiency, stomatal conductance, transpiration rate, and reduced chlorophyll degradation, leading to tolerance from external insult (Haghighi and Pessarakli, 2013). Salt stress is the primary culprit causing significant changes in the epicuticular wax layer.

Interestingly, nano-Si application to strawberry plants resulted in better epicuticular wax structure and thickness as compared to the salt-stressed plant (Avestan et al., 2019). Another work performed on sweet pepper plants (*Capsicum annum* L.) to study the impact of nano-Si to mitigate salt stress observed significant changes in comparison to their bulk counterpart (Tantawy et al., 2015). Nano-Si was supplied to the plants through an irrigation system at low concentrations (1.0 and 2.0 cm^3/L) for weeks, resulting in enhanced leaves and fresh weight. The concentration-dependent effect of SiO$_2$ NPs was also observed on potato plants exposed to different salt stress (NaCl; 50 and 100 mM). The NPs were able to show better stress amelioration at a lower concentration (50 mg/L) and a higher concentration (100 mg/L) (Gowayed et al., 2017). However, lower concentration was found to be more effective. These studies notably suggest a better viewpoint about the positive and negative impact of NPs, contradicting the assumptions of only toxic aspects of NMs. Therefore, it is required to initially study the characteristics of NPs before employing it in any field.

Plant hormones play a vital role during external stress conditions and confer better adaptation to different changing environmental scenarios (Verma et al., 2016; Raza et al., 2019). A plant growth hormone such as Gibberellin has an important role in plant responses against various abiotic stresses including drought, shading, flooding, and low temperature mainly by reducing the plant growth to divert the focus onto withstanding stress response (Colebrook et al., 2014). Plant hormones can also be supplied to the plant by utilizing NMs; for instance, Mesoporous silica NPs (MSN) entrapping abscisic acid were tested on the *A. thaliana* plant. It significantly showed the prolonged release of hormones and further improved the drought resistance ability of the seedlings (Sun et al., 2018).

Titanium Dioxide NPs (TiO$_2$ NPs)

We have described the antioxidative effects of specific NPs that scavenge ROS produced in response to threat or stress in plants, but there are other NPs that exert their effects through other mechanisms involving gene regulation (**Table 1**). For example, TiO$_2$ NP exposure (0.01%) increased the chlorophyll content and biomass by triggering a mechanism of antioxidant enzyme activities, resulting in decreased malondialdehyde and hydrogen peroxide and production of proline and soluble sugars, thus maintaining the osmotic balance (Abdel Latef et al., 2018). Similarly, nano-TiO$_2$ was able to trigger the expression of particular essential non-coding RNA considered to play a vital role in the abiotic stress-resistance mechanism. Frazier et al. observed the expression of 11 conserved miRNA in response

to TiO$_2$ NPs (0.1, 1, 2.5, and 5%) in tobacco seedlings that are responsible for rescuing plants from heavy metal stress (Frazier et al., 2014).

Water deficit is a severe issue for plant cultivation as it leads to a loss in vigor and causes severe damage to crops. Nano-TiO$_2$ can improve the hydration status of the plant by increasing the activity of the nitrate reductase (NR) enzyme, which, in turn, enhances the accumulation of osmolytes. The increased NR enzyme activity results in nitric oxide (NO) production that ultimately induces proline and glycine betaine synthesis (Khan et al., 2020). TiO$_2$ NPs tend to show both enzymatic as well as a non-enzymatic defense system against stress in plants. Interestingly, TiO$_2$ NPs are acknowledged for the regulation of other enzymes, such as glutamate hydrogenase, glutamine synthase, and so on, thereby, accumulating more nutrients and also essential oil production (Ahmad et al., 2018). In this regard, Gohari et al. carried out a greenhouse experiment to evaluate the effect of nano-TiO$_2$ (0, 50, 100, and 200 mg L^{-1}) on Moldavian balm (*Dracocephalum moldavica* L.) plants grown under exacerbated salinity stress (0, 50, and 100 mM NaCl). The TiO$_2$ treated plants (100 mg/L) showed a profound effect on the production of essential oil content (1.19%): geranial, z-citral, geranyl acetate, and geraniol under normal conditions. This implicated protection of aromatic plants against the stress condition by directly modifying their essential oil production profile and composition (Gohari et al., 2020). Karamian et al. carried out another study on medicinal plants showing that drought stress was mitigated by supplying methyl jasmonate (200 μM), salicylic acid (100 μM), and TiO$_2$ NPs (20 ppm). The results suggest that it increased water stress tolerance through activation of enzymatic and non-enzymatic antioxidant defense systems (Karamian et al., 2020).

Nano Pesticides

As more than half of the worldwide population rely on plants and their products for survival, it is a significant concern to enhance plant productivity as well as maintenance of their health. As several biotic and abiotic factors include pathogens, nutrient deficiency, or soil/air pollution, respectively, all equally can affect the health of the plant via inducing damages that, consequently, lead to decreased crop and fruit yield. Frequently, plant disease is caused by a broad range of disease-causing organisms (or pests). Thus, it is an immediate requirement to keep them from causing more plant wilting. Insects are crucial matters in agriculture as they demolish crops and overrun stored food, consequently causing the worsening quality of food and transmission of plant diseases. As per the definition of the U.S. Environmental Protection Agency, pesticides are substances that deliberately prevent, repel, and demolish any pest (**Figure 3**).

Pesticides are used to enhance and improve the crop yield and efficiency by protecting plants from damaging factors, including plant diseases and insects (Jampílek and Králová, 2017). However, it has been found that the use of pesticides is lethal and toxic for the environment; most of them are hazardous and lethal to human and animal health. Therefore, many pesticides are banned by state or international authorities. This involves several significant and vital issues, including

indiscriminate use of pesticides at a high concentration that harms the ecosystem, increasing bioaccumulation, making the soil infertile, and disrupting its microbiota (Meena et al., 2020). Some issues must be taken into consideration to increase agronomic productivity and efficiency and reduce the environmental effect (**Figure 3**).

The synthesis of effective and safe pesticides is tricky and expensive, but nanotechnology provides a novel and improved solution (Sasson et al., 2007). Nanotechnology already has a significant impact on pharmacy (drug delivery). With the recent developments in the agriculture and food sector, it is promising. Nanotechnology is not restricted to applications for plant protection against pests, but expands to minimize waste, monitor of plant growth, guarantee enhanced food quality, and secure rising of global food production (Jampílek and Králová, 2017). The most frequent trials in nano pesticides are nano herbicides, nano insecticides, nano nematocides, and nano fungicides (**Table 2**).

The best example of a nano insecticide is nanostructured alumina (NSA), which is nanoengineered material that works as an insecticide. It is synthesized through the oxidation of metal, which exhibits a fixed electric charge. Advance nanotechnology designed NSA in such a way so it can combat insects by taking advantage of its system. Insects show electric charges, which are created through triboelectrification. Tribo-charge is a type of contact electricity or electrification generated by two non-conductive bodies or material when they come in contact through friction. Furthermore, an exciting mode of action of NSA takes advantage of insect tribo-charging and is completed in two sequential mechanistic steps. Primarily, negatively charged NSA particles initiate interaction with a positive charge of the insect through strong electrical bonding. This interaction causes dehydration of the insect through the potent sorptive property of the NSA particle, which detaches insects' cuticle insect layer, a fibrous composite of chitin and results in the death of the insect due to dehydration. As hypothesized, the insecticidal property of NSA powder or particle is based on the attachment of the particle to the cuticle of the insect, which further disturbs the water balance and leads to ambient increased humidity. The strong insecticidal efficacy of NSA relies on its small size, intrinsic electric charge, sorbative prosperity, and large surface area (Stadler et al., 2018; **Figure 4**).

Moreover, engineered nano pesticides are assisting the conventional cotton and insect-resistant transgenic (Bt cotton) crop, which was designed to combat the bollworm. Insecticidal activity of Cu NPs at a low dose (10 mg/L) has the potential to upregulate the expression of exogenous microbial protein from Bacillus thuringiensis coded through the Bt toxin in plant tissue to improve resistance against the bollworm (Zhao et al., 2020; **Table 2**). During spot disease in tomato plants, TiO_2 and ZnO NPs, photochemically active, act as antimicrobial agents. When TiO_2 and ZnO NPs (photochemically active) are exposed to light, they generate excited electrons, which, in the presence of oxygen, synthesize superoxide radicals through direct electron transfer. Using photochemically active TiO_2, NPs are engineered to have antimicrobial properties and have a great impact on agriculture as nano pesticides. It has extensive photocatalytic activity and

higher antibacterial potential against *X. perforans,* which causes spot disease in tomato plants (Paret et al., 2013).

Furthermore, the packaging of conventional pesticides with NPs or polymers is highly demanding in the area of the pesticide industry as they are anticipated to address these issues by enhancing pesticide efficiency, increasing production, reducing excess runoff by slow release of active ingredients over a prolonged period (Nuruzzaman et al., 2016), and ultimately protecting the environment. This new field of research comprises the study of the interaction of NPs with insects to improve existing pest control management and provide advanced nanoformulations that remain stable, quickly penetrate the organism, are delivered at the targeted site, are cost-effective, and are more active during field applications. Nanoformulation or nano carriers act as the vehicle to transport and control delivery or release of the active compound, which presents in its core, and is used to conserve an adequate amount of compound during the whole period of insect growth (from the transition from larva to the maturity stage). For instance, sustainable nano carrier construction of chitosan liposome, which coats the inner core, consists of etofenprox or alpha-cypermethrin. Similarly, different types of NMs and nanoformulations of conventional pesticides have been developed that show a significant impact on pest control (**Figure 4**).

Nanoemulsions

Nanoemulsions refers to the oil-in-water emulsion in which pesticide is dispersed as nanosized droplets in water. The main advantage of producing nanoemulsions is to increase the solubility of pesticidal active ingredients. The nanoemulsions of neem oil show that smaller droplets are efficiently taken up as LC50 is found to be decreased with droplet size (Anjali et al., 2012). However, the higher efficacy of the permethrin nanoemulsion than that of permethrin macroparticles against yellow fever mosquito (*Aedes aegypti*) is indicative of its enhanced uptake (Kumar et al., 2013). In one study, it is reported that Emamectin-benzoate nanoemulsion is more effective against the Asian rice borer (*Chilo suppressalis*) compared to coarse emulsions (Fan et al., 2010). In some reports, no significant results were obtained with pesticide colloids, for example, no significant difference in LC50 values was found for nanoemulsion of Chlorpyrifos and a commercially available coarse emulsion against cotton bollworm (*Helicoverpa armigera*) (Qi-liang et al., 2006). Another important aspect is their controlled or slow release from the colloidal formulations that result in more sustained and prolonged exposure (**Figure 4**).

Polymer Nano Pesticides

These are polymer-based nanocarriers for encapsulating pesticides that act as a protective reservoir containing polysaccharides and polyesters. In addition to this, they tend to increase dispersion in aqueous media, facilitating the slow and controlled release of pesticides. The polymer nano pesticides have gained lots of attention as they are flexible to design, biodegradable (corn oil, beeswax, and cashew gum), and biocompatible. Polymer-based nanoformulations such as

TABLE 2 | Different types of NPs employed for the generation of nano pesticides, their composition, benefits, target pests, and examples of active components.

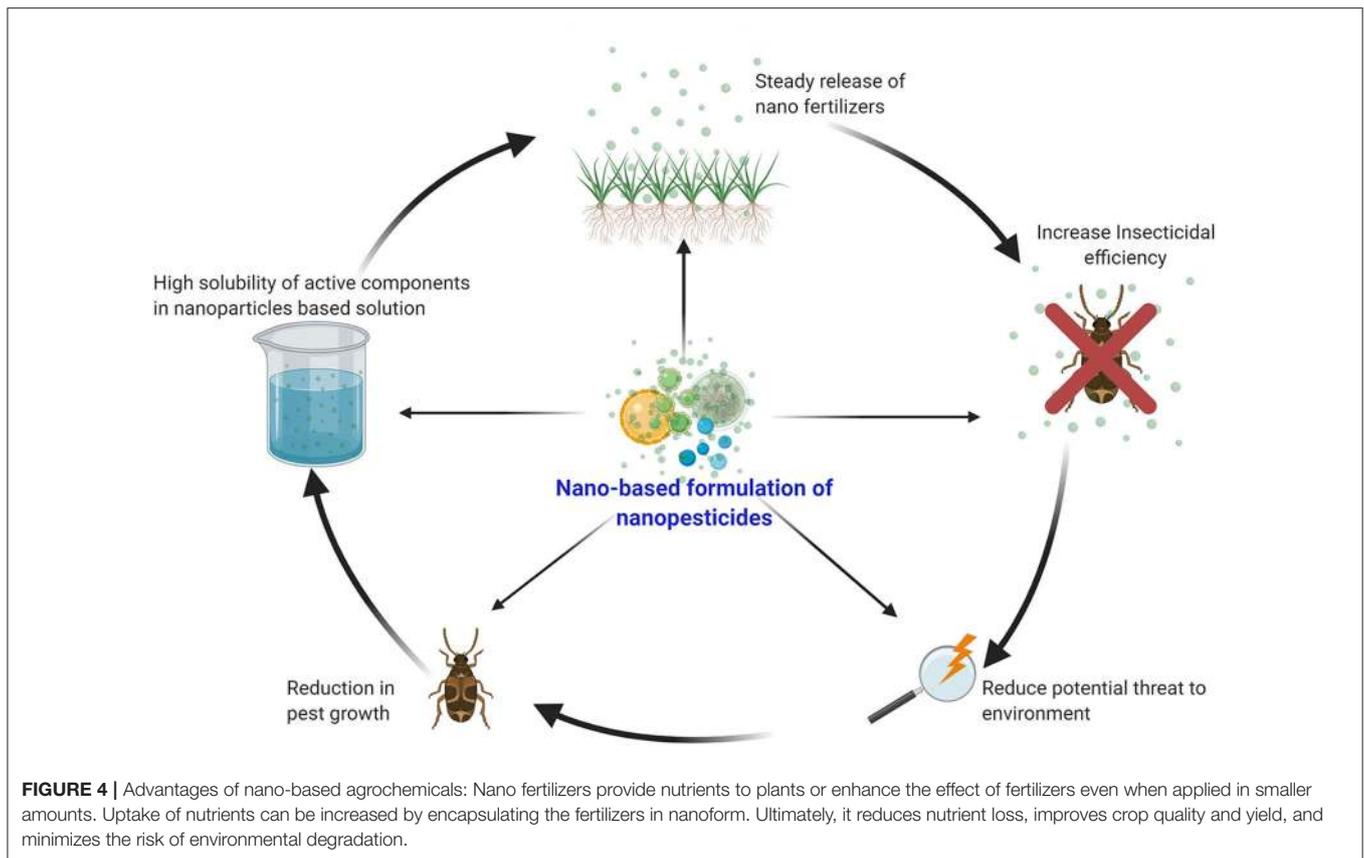| S.No	Nanomaterial	Name nanoparticles	Concentration	Pest	Plant disease	Advantage	References
1	Ag-Based NPs	DNA directed silver (Ag) nanoparticles grown on graphene oxide (GO)	16 mg/L	*Xanthomonas perforans*	Bacterial spot of tomato	Significantly decreased the activity of cultured *Xanthomonas perforans*	Ocsoy et al., 2013
2		AgNPs	(30–150 mg/mL)	*Meloidogyne* spp.		99% of the nematodes died within 6 d	Cromwell et al., 2014
3		AgNPs	150 mg/mL	*Meloidogyne* spp.		Reduced the number of nematodes by 82 and 92% at day 2 and day 4, respectively, in field	Cromwell et al., 2014
4		*Serratia* sp. biosynthesized AgNPs		*Bipolaris sorokiniana*	The spot blotch pathogen of wheat	Biosynthesized AgNPs exhibited strong antifungal activity	Mishra et al., 2014
5		Turnip leaf extracted green-synthesize AgNPs	(~16 nm)	*Gloeophyllum abietinum, G. trabeum, Chaetomium globosum,* and *Phanerochaete sordida*	Several wood-degrading fungi	Showed broad spectrum antifungal activity against several wood-degrading fungi	Narayanan and Park, 2014
6		*Artemisia absinthium* extracted green-synthesize AgNPs	10 mg/L	*Phytophthora*	Phytophthora infection	Suppressed Phytophthora infection on plants and improved plant survival	Ali et al., 2015
7	Cu-Based NPs	Cu(OH)$_2$NPs (Kocide 3000)	1,000 mg/L	*Escherichia coli* and *Bacillus subtilis* as well as the plant fungal pathogens *F. oxysporum, C. lunata, A. alternata,* and *P. destructiva*		Antibacterial efficiency of CuNPs vs. the traditional fungicide bavistin (Devistin, carbendazim 50% WP) demonstrated the better performance of CuNPs	Yoon et al., 2007
8		Cu$_3$(PO$_4$)$_2$·3H$_2$O nanosheets	10 mg/L	*Fusarium oxysporum f.*sp. *niveum*	Suppress root fungal disease in watermelon (*Citrullus lanatus*)	58% decrease in disease progression	Borgatta et al., 2018
9		CuNPs and K$_2$SiO$_3$NPs	50 mg/L CuNPs + 184 mg/L Si; 50 mg/L CuNPs + 460 mg/L Si; 250 mg/L CuNPs + 184 mg/L Si; and 250 mg/L CuNPs + 460 mg/L Si	*Clavibacter michiganensis*	Reducing the severity of *C. michiganensis* infection on hydroponically cultivated tomato plants	Combined application of the two particle types stimulated the levels of the enzymatic and non-enzymatic metabolites essential for the defense of tomato plants and thus increased the tolerance of *C. michiganensis*	Cumplido-Nájera et al., 2019
10		CuONPs	10 mg/L	*S. littoralis*	Insecticidal activity on Bt-transgenic cotton and conventional cotton	Enhanced the expression of exogenous genes encoding Bt toxin in cotton plant tissues	Ayoub et al., 2018
11		CuNPs	Lethal concentration 50 (LC50) of 232 mg/L after 3 d, whereas for CaO NPs an LC50 of 129 mg/L was achieved 11 d post-treatment	*S. littoralis*	Insecticidal activity on Bt-transgenic cotton and conventional cotton	Cu NPs exhibited faster entomotoxic effects than achieved with CaO NPs	Ayoub et al., 2018
12	Carbon-Based NPs	SWCNTs, multiwalled carbon nanotubes (MWCNTs), graphene oxide (GO), reduced graphene oxide (rGO), fullerene (C60)	62.5, 125, 250, and 500 mg/L	*Fusarium graminearum* and *Fusarium poae*	At 500 mg/L, C60 inhibited the spore germination of *F. graminearum* but not with *F. poae*	Strongest antifungal activity was exhibited by SWCNTs (500 mg/L), followed by MWCNTs (500 mg/L), GO (500 mg/L), and rGO (500 mg/ L), whereas the AC at this tested concentration range showed no antifungal effect. These particles induce inhibition of water uptake and the induction of plasmolysis	Wang et al., 2014

(Continued)

TABLE 2 | Continued

S.No	Nanomaterial	Name nanoparticles	Concentration	Pest	Plant disease	Advantage	References
13	Ti-Based NPs	TiO_2 NPs (Photochemically active)	500–800 mg/L	*X. perforans*	The pathogen that induces spot disease in tomato plants	High photocatalytic activity and antibacterial potential to reduced bacterial spot severity	Paret et al., 2013
14	Ce-Based NPs	CeO_2 NP	50 and 250 mg/L by root and foliar path	*Fusarium wilt*	Mediated suppression of in tomato	250 mg/L CeO_2 NPs significantly reduced disease severity, by 53% and 57%, respectively	Adisa et al., 2018
15	Mg-Based NPs	MgONPs	0.1, 0.5, 0.7, or 1% (growth media: 50% vermiculite and 50% perlite)	*Ralstonia solanacearum*	Resistance of tomato plants to Ralstonia solanacearum	The pretreatment of tomato roots with MgONPs suspension (0.1, 0.5, 0.7, or 1%) significantly reduced the incidence of disease. The mechanism included the upregulation of salicylic acid-inducible PR1, jasmonic-acid-inducible LoxA, ethyleneinducible Osm, and systemic-resistance-related GluA	Imada et al., 2016
16		MgONPs	200 or 250 mg/L	*R. solanacearum*	Induced tobacco bacterial wilt	Effectively suppressed *R. solanacearum*, which induced tobacco bacterial wilt. Proposed mechanism included physical injury of cell membranes and ROS accumulation	Imada et al., 2016
17		Synthesized $Mg(OH)_2$ NPs		*X. alfalfae, Pseudomonas syringae,* and *E. coli*		Inhibited the growth of *X. alfalfae, Pseudomonas syringae,* and *E. coli* within 4 h. The killing activities of $Mg(OH)_2$ NPs were comparable to those of Kocide 3000, thus demonstrating their potential as a Cu alternative	Huang et al., 2018
18	Si-Based NPs	SiNPs	15 kg/ha/20–40 nm	*Aspergillus* spp.	Phytopathogen resistance of maize	Triggered the pregulation of phenolic compounds, resulting in the greater resistance of the plants to *Aspergillus* spp.	Suriyaprabha et al., 2012
19		Mesoporous silica nanoparticles (MSNs) with a chitosan coating (CTS-MSNs) or without	36 nm, 500 mg/L	*Fusarium wilt*	Suppress Fusarium wilt in soil-grown watermelon	Both MSNs and CTS-MSNs reduced disease severity, by 40 and 27%, respectively	Buchman et al., 2019
20	Mn-Based NPs	MnONP	1 mg/L /40 nm	*Fusarium oxysporum f.*sp. *lycopersici*	Tomato disease	Reduced disease estimates [area under the disease progress curve (AUDPC)] by 28% in plants grown in soil	Elmer and White, 2016

(Continued)

TABLE 2 | Continued

S.No	Nanomaterial	Name nanoparticles	Pest	Plant disease	Advantage	References
21	Nanoformulations of conventional pesticides Cellulose/silica nanocomposites	Tebuconazole	Rust and molds	Leaf senescence and decay	50% improvement in release rate	Mattos and Magalhães, 2016
22	Porous hollow silica	Validamycin	–	–	Loading capacity improved up to 36%	Liu F. et al., 2006
23	Calcium carbonate	Validamycin	*Rhizoctonia solani*		Controlled release up to 2 weeks	Qian et al., 2011
24	Porous hollow silica	2,4-dichlorophenoxyacetate	–	–	Improved herbicide activity period	Bin Hussein et al., 2005
25	Lignin	Diuron	–	–	Improved controlled release rate	Yearla and Padmasree, 2016
26	Other nanomaterials	Silver (Ag) NPs	*Xanthomonas campestris* pv. campestris	Bacterial blight	Significant reduction of bacteria	Rajesh et al., 2012
27		Ag core-DHPAC shell nanocluster	*Phytophthora capsici, Phytophthora nicotianae,* and *Phytophthora colocasiae*	Fungal disease	Up to 80% of growth inhibition	Ho et al., 2015
28		Chitosan NP	*Rhizopus* sp., *Colletotrichum capsici, Colletotrichum gloeosporioides,* and *Aspergillus niger*	Disease in Chile	Delayed mycelia growth	Chookhongkha et al., 2012
29		Chitosan NP	*Alternaria alternata, Macrophomina phaseolina,* and *Rhizoctonia solani*	Fungal disease	Inhibited spore germination	Saharan et al., 2013
30		Iron oxide (FeO) NP	*R. solani, B. cinerea,* and *F. oxysporum*	Fungal disease	60–80% of fungal inhibition	Chhipa and Kaushik, 2015
31		Copper (Cu) NP	*Fusarium* sp.	Fungal disease	Antifungal activity	Bramhanwade et al., 2016
32		Copper (Cu) NP	*Xanthomonas axonopodis* pv. punicae	Pomegranate bacterial blight	Inhabited bacterial growth	Mondal and Mani, 2012
33		Copper (Cu) NP	*Phytophthora infestans*	Disease in tomato	Active at low concentration of antifungal agent	Giannousi et al., 2013

FIGURE 4 | Advantages of nano-based agrochemicals: Nano fertilizers provide nutrients to plants or enhance the effect of fertilizers even when applied in smaller amounts. Uptake of nutrients can be increased by encapsulating the fertilizers in nanoform. Ultimately, it reduces nutrient loss, improves crop quality and yield, and minimizes the risk of environmental degradation.

nanogels, nanospheres, or nanofibers could be a better substitute (Nuruzzaman et al., 2016).

Solid NPs as Nano Pesticides

Some NPs that are considered to be antibacterial/pesticidal agents instead act only as nanocarriers, for example, inert dust of alumina, silica, and clays that damage the inner wax coating of the insect cuticle, which, in turn, loses water and dies due to desiccation. This mode of action is considered safer as it is unlikely that insects will develop resistance (Shah and Khan, 2014). SiNPs cause damage to the protective epidermis layer by being physio-sorbed on the lipids, thus causing the death of the insects (Barik et al., 2008). Nanostructured alumina was discovered by Stadler et al. (2010) as an insecticide against two grain pests, *R. dominica* and *S. oryzae*. The thin sheets of silicate materials are nanoclays that are produced from volcanic ash. They have been efficiently used as a carrier for controlled release of a potent herbicide 2,4-dichlorophenoxyacetate bin (Bin Hussein et al., 2005).

Nanoherbicides

Weeds are considered to be the biggest threat for damaging crops in a greater quantity by utilizing nutrients that would otherwise be available to plants. Conventional methods, including removing weeds by hand, for eradicating weeds is time-consuming and requires a lot of effort. Many herbicides are currently available in the market that have the potential

to kill weeds in a field but also cause harm to the crops and decline the soil fertility. Nanoherbicides can be a better, eco-friendly alternative for effective weed control without leaving any toxic residues in the soil (Pérez-de-Luque, 2017; **Table 2**). Constant use of the same herbicide for a more extended period could lead to resistance in the weeds. Poly (epsilon-caprolactone) (PCL) nanocapsules have been used as a carrier system for the conventional herbicide atrazine. The atrazine-containing nanocapsules showed more potent post-emergence herbicidal activity on mustard plants than a commercial atrazine formulation (Oliveira et al., 2015). Chitosan NPs were prepared by cross-linking through disulfide bonds of diuron for its controlled delivery based on the concentration of glutathione (Yu et al., 2015).

Nanofungicides

Fungal diseases are the most common and account for more than 70% of damage to major crops such as rice, wheat, barley, groundnut, and cotton (Godfray et al., 2016). These diseases affect society by causing severe loss to crop yield and the economy. Conventional fungicides work to curb these losses but, on the other hand, target non-specific living organisms and cause imbalance to the biodiversity. Therefore, we need to look for alternate approaches to achieve better precision in fungal disease management (Patel et al., 2014). One of the best approaches is the development of NPs as an effective strategy against fungal

pathogens. AgNPs, owing to their antimicrobial properties, are widely used for disinfection purposes (Baker et al., 2005). An experiment was conducted to check the effectiveness of AgNPs and Ag ions on plant-pathogenic fungi *Bipolaris sorokiniana* and *Magnaporthe grisea*. The ionic and nanoparticulate forms were effective against fungi and significantly reduced disease severity when applied for 3 h (Jo et al., 2009). CuNPs and AgNPs can both suppress the growth of two fungal pathogens *Alternaria alternata* and *Botrytis cinerea* (Ouda, 2014). ZnO NPs and MgO NPs show antifungal activity against *Alternaria alternate, Rhizopus stolonifer, Fusarium oxysporum,* and *Mucor plumbeus* (Wani and Shah, 2012). An MWCNT-g-PCA hybrid material encapsulated two conventional pesticides, zineb and mancozeb, which was confirmed to be a more potent fungicide against *A. alternate* (Sarlak et al., 2014).

Nano Fertilizers

Currently, agriculture all across the globe faces a broad spectrum of challenges, such as nutrient deficiency, stagnation in crop yields, diminishing soil organic matter, low water availability, nutrient deficiency in the soil, decreased land area due to urbanization and land degradation, and labor shortages (Godfray et al., 2010). The application of nanoscience and nanotechnology is increasing tremendously, and novel methods are continuously being proposed to produce novel and desirable materials for crop production and management (**Table 3**). It is one of the most influential ideas of the evolving science of precision agriculture in which farmers efficiently make use of fertilizers and other inputs. The uncontrolled population has prompted the enormous production of conventional fertilizers to increase food production and crop protection, but this ultimately decreases the soil fertility and quality of food. These chemical fertilizers not only add to the tribulations of the subtle ecosystem, but also affect human health as they remain unused. The global demand for fertilizers is expected to rise in the coming years, according to a report submitted by the Food and Agricultural Organization of the United Nations. Therefore, it is imperative to involve intelligent strategies for sustainable agriculture, such as nanotechnology. Nano fertilizers are environmentally friendly fertilizers or smart fertilizers with the potential to increase the application rates of fertilizers and reduce the loss of nutrients from it, mainly phosphorous and nitrogen (Dimkpa and Bindraban, 2017). It offers the gradual and controlled release of nutrients to the targeted site, which helps to prevent the contamination of water bodies and the environment (Dwivedi et al., 2016; **Figures 2, 3**).

Nano fertilizers are those that either provide nutrients to plants or enhance the effect of fertilizers even when applied in smaller amounts (Rameshaiah et al., 2015). Uptake of nutrients can be increased by encapsulating the fertilizers in nano form that ultimately reduces nutrient loss, improves crop quality and yield, and also minimizes the risk of environmental degradation (**Figure 2**). The foliar application of these nano fertilizers is also demonstrated to mitigate the stress in plants (Tarafdar et al., 2012). Nano fertilizers can be divided into three categories based on the nutritional requirements of the plants: (1) macronutrient nano fertilizers, (2) micronutrient nano fertilizers, and (3) nanoparticulate nano fertilizers (Chhipa, 2017). Macronutrient nano fertilizers are composed of a combination of elements, such as potassium (K), magnesium (Mg), nitrogen (N), calcium (Ca), and phosphorus (P). It is estimated that the total consumption of macronutrient fertilizers is projected to increase to 263 million tons (Mt) in 2050, thus showing a critical need for these fertilizers in the agricultural sector. Delfani and his group tested the efficiency of Mg and Fe NPs on the growth of black-eyed peas (*Vigna unguiculata*) by foliar application and observed enhanced seed weight and photosynthetic ability that, in turn, increased the yield (Delfani et al., 2014). The Ca NPs, together with humic acids, improved seedling growth in peanuts (about 30% increase) with dry biomass reaching 5.78 g per plant (Liu et al., 2005). The synthesized hydroxyapatite $[Ca_5 (PO_4)_3 OH]$ NPs of size 16 nm significantly enhanced the growth rate and yield of soybeans (*Glycine max*) in comparison to control. These studies suggest that NPs can be applied as potent fertilizers for field crops (Liu and Lal, 2015). For more detail, please refer to **Table 3**.

Plant micronutrients consist of molybdenum (Mo), copper (Cu), iron (Fe), nickel (Ni), manganese (Mn), and Zinc (Zn), and compared to macronutrients, they are required in much smaller amounts for the healthy growth of crops. Micronutrients applied as composite formulations are more effective in providing enough nutrients and cause less environmental degradation. Micronutrients packed in NPs enhance the nutrient bioavailability and fertilizer use efficiency relative to other conventional ions and salts (Dimkpa and Bindraban, 2016). The composite of three micronutrients NPs (ZnO, CuO, and B_2O_3) has been successfully established for agronomic fortification to mitigate drought stress in soybean plants (Dimkpa et al., 2017a). Nanoparticulate fertilizers contain other NPs, such as CNTs, TiO_2, and SiO_2, that enhance the growth of plants. The mixture of TiO_2 and SiO_2 increased nitrogen fixation, growth enhancement, and improved seed germination in soybeans (Lu et al., 2002; **Table 3**).

Molecular Mechanism of Nano Fertilizer Uptake, Translocation, and Action

Use of NM as nano fertilizer is possible due to its smaller size than the pore size of the plant cell wall (up to 20 nm), which contributes to nutrient uptake. Nano fertilizers can directly apply to soil and/or leaves. Therefore, there are two significant modes of application of nano fertilizer. First is foliar entry, and second is root entry. Spray on the trough cuticle, stromata, hydathodes, lenticels, and wounds leads to the foliar entry, and root tips, lateral root, root hairs, and rhizodermis provides the root entry. Foliar applications of nano fertilizer prefer or can be done during unfavorable soil and weather conditions (**Figure 1**).

Additionally, this mode of application promotes the direct entry of nutrients into the plant leaf system, simultaneously reducing the wastage of fertilizer. Hence, foliar application of nano fertilizer leads to higher NUE and also gives a rapid response to the growth of crops or plants (Mahil et al., 2019). Foliar entry is facilitated by nano-pores, the base of the trichome and stromal opening in leaves, easing NP uptake and their transport inside of leaves. For instance, in faba beans (*Vicia faba*) and more (in *C. arabica* below 2.5 nm and *P. cerasus* below

TABLE 3 | Different types of NPs employed for the generation of nano fertilizers, their composition, benefits, and examples of active components.

S.No	Engineered metal nanomaterials	Nano fertilizer	Concentration/size	Plant	Output/ advantage	References
1	Fe-Based NPs	FeOXNPs	Seedlings were cultivated in aqueous medium spiked with 5–20 mg/L	Lettuce (*Lactuca sativa*)	Significantly increased the shoot length of lettuce, by 12–26%	Liu et al., 2016
2		Fe_2O_3NPs	30–60 mg/L	Soybean (*Glycine max* L., Oxley)	Significantly increased the chlorophyll content of hydroponically cultivated soybean	Ghafariyan et al., 2013
3		γ-Fe_2O_3	Cultivation of maize seedlings in a hydroponic solution containing 20 mg/L	Maize (*Zea mays*)	Significantly increased the germination rate and the root length, by 27.2 and 11.5%, respectively. Even at an extremely low dose, iron oxide NPs exert positive effects on plant growth	Li et al., 2016
4		α-Fe_2O_3NPs	Presoaking the plants with the particles at a dose as low as 5.54×10–3 mg/L	Legumes	Significantly increased root length, by 88–366%. Effectiveness of Fe_2O_3NPs as a replacement for traditional Fe-based fertilizers	Palchoudhury et al., 2018 Rui et al., 2016
5		Citric-acid-coated nano-Fe_2O_3		Soybean	Foliar spray of citric-acid-coated nano-Fe_2O_3 significantly enhanced root length and the photosynthetic rate	Alidoust and Isoda, 2013
6		γ-Fe_2O_3	Plants were cultivated in soil spiked with 2 mg/kg concentrations of γ-Fe_2O_3 (20 nm) for 38 d	Peanut (*Arachis hypogaea*)	Significantly enhanced their rate of photosynthesis and their biomass	Alidoust and Isoda, 2013
7	Zn-Based NPs	ZnONPs		Mung bean (*Vigna radiata*)	Foliar application of the particles increased the biomass of the roots and above-ground tissues of the seedlings	Dhoke et al., 2013
8		ZnONPs or Zn salt amendment		Sorghum (cereal)	Efficacies of two exposure pathways (soil and foliar). Foliar application of both ZnO and Zn salt significantly increased sorghum productivity and grain nutritional quality under both low and high NPK input (NPK indicates nitrogen, phosphorous, and potassium)	Dimkpa et al., 2017b
9		ZnONPs	Concentrations ranging from 50 to 2,000 ppm/(25 nm)	Maize	At a concentration of 1,500 ppm, ZnONPs significantly increased the germination percentage (by 80%) and the seedling vigor index. The highest grain yield (3,298 kg/ha) was obtained with ZnONPs at a dose of 400 ppm. Besides its beneficial role in plants under non-stress conditions, ZnO nanoparticles also improved plant performance under salinity stress, drought, and Cd stress	Subbaiah et al., 2016
10	Cu-Based NPs	Cu-chitosan NPs	0.04–0.12%	Maize	Enhanced maize seedling growth by increasing both the activity of α-amylase and the starch content	Saharan et al., 2016
11	Mg-Based NPs	MgNPs	Foliar-sprayed of a dose of 0.5 g/L	Black-eyed pea	Significantly increased photosynthesis and the biomass of the plants. However, the MgNPs altered cell membrane permeability	Delfani et al., 2014
12		MgNPs	Foliar spray of 20 mg/L (<5.9 nm)		Increases in root length, tip number, and root biomass. The mechanism was attributed to the MgNP-induced enhancement of solar energy absorption of the leaves	Rathore and Tarafdar, 2015
13		MgONPs	50, 150, and 250 mg/L	Tobacco	Improved SOD and POD activities in grown in matrix media	Cai et al., 2018

(Continued)

TABLE 3 | Continued

S.No	Engineered metal nanomaterials	Nano fertilizer	Concentration/size	Plant	Output/ advantage	References
14	Mn-Based NPs	MnNPs and MnSO$_4$	Cultivated in Hoagland's nutrient solution with MnNPs or MnSO4 for 15 d at 0.05 mg/L	Mung bean	Significant increases in the fresh and dry biomass (39.0 and 53.6%, respectively) and in root and shoot length of mung bean. Also, greater photophosphorylation and increased oxygen evolution in chloroplasts were treated with MnNPs than in control and MnSO$_4$-treated chloroplasts	Pradhan et al., 2013
15	Mo-Based NPs	MoS$_2$	Foliar application, 32–500 µg/mL (1.5 µm)	Rice	MoS$_2$ (125 mg/L) significantly increased rice plant biomass and the chlorophyll content of the leaves. MoS$_2$ also upregulated the expression of the rice aquaporin gene	Li Y. et al., 2018
16	Si-Based NPs	SiO$_2$ NPs	8 g/L (~12 nm)	Tomato (*L. esculentum Mill.* cv. super strain B)	Significantly enhanced seed-germination-related parameters, such as seed germination, mean germination time, seed germination index, and seedling fresh weight	Siddiqui and Al-Whaibi, 2014
17		Nanosilicon dioxide (SiO$_2$ NPs)	100 mg/L/(10–20 nm)		Improved plant growth rate and productivity in Strawberry plants [grown in coco peat and perlite (2/1, v/v) under salinity stress]	Avestan et al., 2019
18		SiO$_2$ NPs	Foliar spray of 3,200 mg/L	Cotton	Improved growth performance of cotton plants under drought	Shallan et al., 2016
19	MSN-Based NPs	MSNs	0–2,000 mg/L	Wheat and lupin plants	MSNs taken up by the roots were translocated to chloroplasts, where they significantly increased photosynthetic activities. MSNs at doses of 500 and 100 mg/L enhanced seed germination and increased plant biomass, total protein, and chlorophyll content. Even the highest MSNs concentration (2,000 mg/L) did not result in oxidative stress or cell membrane damage	Sun et al., 2016
20	TiO2-Based NPs	Nano-TiO$_2$	0.25%, originated from 1 mL of Ti(OC4H9)4	*Arabidopsis thaliana*	Significantly increased the expression of the light-harvesting complex IIb (LHCIIb) gene and LHCII II in the thylakoid membranes of (grown under agar medium). Also, absorption peak intensity of chloroplasts in the red and blue regions was significantly increased by TiO$_2$ NPs	Ze et al., 2011
21	SWCNT-Based NPs	SWCNTs	5 mg/L	Spinach leaves	Enhanced the photosynthetic activities of whole spinach leaves by 31%, by increasing the electron transfer rate	Giraldo et al., 2014
22	Others	Quantum dots (CQDs)	50, 54.2, and 75 mg/L	Mung bean	Promote acyclic photophosphorylation, ATP synthesis, and oxygen release in isolated mung bean chloroplasts. The resulting enhancement of photosynthesis by accelerated electron transfer rate in thylakoid membranes	Chandra et al., 2014

100 nm), it is demonstrated that nanosized particles (43 nm), deeply buried in the bulk of the leaf interior compartment, which suggests the effectiveness of nano fertilizer to enhance nutrient uptake (Eichert et al., 2008).

As nano fertilizer, it is suggested for higher nutrient use efficiency (NUE) because of its higher ability to pass and deliver the nutrients via nanosized (50–60 nm) pores of plasmodesmata, which usually transports ions between cells (Iqbal, 2019). Furthermore, plant root entry also shows significant passage for nutrient uptake, such as being highly porous to nano fertilizer compared to conventional fertilizer or manure. Demonstration using fluorescently labeled monodispersed mesoporous silica NPs suggest they amazingly describe the mechanism of uptake and translocation of the NP. NPs penetrate the root through symplastic and apoplastic pathways and passes to the xylem tissue to areal regions of the plant, such as the leaves and stem (Sun et al., 2014). For instance, ZnO and CeO$_2$ NPs are illustrated by tracing travel patterns from the entrance into the ryegrass root cells and further up to the vascular tissues in soybeans (*Glycine max*) (López-Moreno et al., 2010). Once entered into the cell, these particles take the way through apoplastically or symplastically, where they travel through the plasmodesmata of one cell to another and finally reach the cytoplasm. In the cytoplasm, they begin to distribute to different cytoplasmic organelles and participate in various metabolic pathways of cells. Also, a higher uptake of NPs in the hydroponic medium as compared to plants grown in the sand has been noticed (Solanki et al., 2015). Hence, nano fertilizers have great potential to transport and deliver nutrients via a smaller channel of plasmodesmata (50–60 nm) from cell to cell. Therefore, higher NUE and less nutrient loss during entrance to transport by nano fertilizer results in higher productivity, ∼6–17%, and increased nutritional quality of field crops and plants (Iqbal, 2019; **Figure 1**).

SENSING SYSTEM WITH NPs

The uncontrolled use of pesticides, fertilizers, and heavy metals in agricultural practices needs to pay attention to minimize the loss to the environment. Regular monitoring of the health status of soil and possible occurrence of any disease must be done with the help of emerging technologies. Accurate sensing systems must be developed that should be handy and portable for real-time monitoring of large field areas. Nanotechnology could enhance the performance of any biosensor to agree with its real application in agriculture. Remarkable progress in the nanofabrication technology and sensitive analytical techniques enables responsive sensor development. Nano sensors could demonstrate their potential in many areas, such as crop cultivation and harvesting, pathogen detection, and soil parameters (pH and nutrients), to name a few. NPs have unique surface chemistry, electrical and thermal characteristics, enhanced sensitivities, and enhanced detection limits that make them suitable for better sensing systems (Yao et al., 2014).

NP-Based Biosensor for Pesticide Residue Detection

Traditional methods often employed for pesticide detection, such as high-performance liquid chromatography and GC/MS, are highly reproducible but suffer from low detection limits and require more efforts (sample collection, extraction, analysis) and well-equipped laboratories (GC/MS pesticide detection). The pesticide, heavy metals, and other pollutants present in water and soil are detected by various NMs, such as metal NPs, graphene, CNTs, and QDs (Zhang and Fang, 2010). The use of NMs adds the further advantages of high sensitivity, low sample requirement, and faster detection. The binding of the target molecule with that of the biosensor can be measured by various direct and indirect means, such as recording changes in color, electrical potential, or fluorescence. Another strategy is array-based in which biomolecules can be fixed to a substrate and allows simultaneous measurement of multiple analytes (Ghormade et al., 2011). NMs such as cadmium telluride (CdTe) QDs were employed for the detection of 2,4-dichlorophenoxyactic acid based on a fluoroimmunoassay-based sensing system (Vinayaka et al., 2009).

Furthermore, the fluorescent property of QDs, owing to their high photostability and size-tunable emission properties (Vinayaka and Thakur, 2010), can also be exploited for the detection of other harmful pesticides, such as atrazine (Cummins et al., 2006), pyrethroid (Kranthi et al., 2009), and methiocarb (Hua et al., 2010). The optical-based immunosensors employ several NMs, including QDs and AuNPs, that give enhanced signal amplification. Chen et al. employ QDs conjugated with streptavidin for detecting the pesticide chlorpyrifos in drinking water (Chen et al., 2010). AuNPs can be used for detecting onsite pesticides found in water coming from agricultural fields and other resources (Lisha and Pradeep, 2009). AuNP function is realized for immunochromatographic test strips for the detection of different pesticides. The authors report a single-step, Au-based, lateral-flow immunoassay strip assay for the simultaneous detection of triazophos and carbofuran. Most of the pesticides are inhibitors of an enzyme acetylcholinesterase (AChE), which is crucial to human health. This enzymatic reaction can be utilized to make biosensors; for example, the concentration of a pesticide was measured using a localized surface plasmon resonance fiber-optic biosensor, which monitors AChE inhibition (Guo et al., 2009). The enzyme was immobilized on the surface of AuNPs and alters the light on inhibition with a pesticide (e.g., paraoxon) that enables its quantification.

NPs for Plant Pathogen Detection

NMs can be applied as a rapid diagnostic tool or a biomarker against various plant pathogens and can be used either directly or indirectly for pathogen detection or used as an indicator for detecting specific diseases. AuNP-based immunosensors were utilized for detecting Karnal bunt (*Tilletia indica*) disease in wheat using surface plasmon resonance (Singh et al., 2010). Fluorescence SiNPs, combined with Ab, were utilized to detect *Xanthomonas axonopodis* pv. *vesicatoria*, known to cause bacterial spot disease in Solanaceae plants (Yao et al., 2009).

The area has lots of potential but is still in its infancy and has to be realized in real field applications. Another essential strategy is the use of nano-chips, a type of microarray that consists of fluorescent oligo probes to identify hybridization (López et al., 2009). QD fluorescence resonance energy transfer-based immunosensors were developed to detect *Phytoplasma aurantifolia* that causes witches broom disease of lime and showed high sensitivity (100%) and specificity with a detection limit of 5 ca. *P. aurantifolia* per μL (Rad et al., 2012). Whenever plants get an infection with any pathogen, they produce unique volatile signatures (plant volatiles), and the detection of these signature compounds could help to confirm the presence of any pathogen infection in plants. Although the occurrence of *p-ethylguaiacol* released by plants upon infection with fungi *Phytophthora cactorum*, TiO_2 and SnO_2 detected it on screen-printed carbon electrodes through an electrochemical sensing system (Fang et al., 2014). Both the NPs exhibited high sensitivity (174–188 μA cm^{-2} mM^{-1}) with 35–62 nM as a low limit of detection (Fang et al., 2014).

NP-Based Smart Plant Sensing System

The smart plant sensing system offers precise management of costly agrochemicals (i.e., pesticides, fertilizer, nutrients, and water) and mitigates major plant stress events in a changing climate. Increasing total crop yield requires innovative and high-throughput smart plant sensing approaches for developing plant stress-tolerance varieties and increasing the use of limited resources, such as nutrients and water. The smart nano sensors used for the optimization of crop growth and precisely detecting stress and limited resources can communicate through wireless and optical signals for real-time monitoring of plant health status (Giraldo et al., 2019). Regular monitoring of the health status of plants and possible occurrence of any disease must be done with the help of Raman and infrared spectroscopy that generate low signal-to-noise ratios and involve complicated and costly equipment (Wilson et al., 2015; Altangerel et al., 2017). Recently, remote sensing tools have improved the signal-to-noise ratio for monitoring individual plant health status and can directly communicate with hyperspectral imaging cameras and smartphones with a nanobiotechnology-based smart plant sensing system (Baret et al., 2007; Hatfield et al., 2008; Wolfert et al., 2017; Padilla et al., 2018).

Real-time monitoring of plant resource deficits or stressors is based on crucial signaling molecules (i.e., calcium, ROS, NO, glucose, and sucrose) and plant hormones (i.e., ABA, ethylene, jasmonic acid, and methyl salicylate) by a nanotechnology-based smart sensing system (Kim et al., 2010; Gilroy et al., 2014; Giraldo et al., 2019). NMs, having unique surface chemistry, electrical and thermal characteristics, enhanced sensitivities, and enhanced detection limits, are suitable for better sensing systems for crucial signaling molecules *in vivo* (Yao et al., 2014). These emerging properties of NMs make them fluorescent in low or transparent-background windows and ultra-low photobleaching of living tissue and allow the detection of analytes with high spatiotemporal resolution down to the single-molecule level and millisecond time scales (Guo et al., 2014; Hong et al., 2015).

QDs are fluorescent NM sensors used for highly glucose selective (500–1,000 μM) emission ranges from the visible to the near-infrared (nIR) for assessing plant productivity and stress (Li J. et al., 2018). Short-lived signaling molecules, such as calcium, ROS, NO, glucose, and nitroaromatics, can be real-time monitored, applying SWCNT sensors in the selected region of the leaf that can reported fluorescence intensity with high spatiotemporal resolution (seconds) (Giraldo et al., 2014, 2015; Wong et al., 2017). Analytes bind with the SWCNT sensor humic phase coating, both altering the nIR fluorescence intensity or shifting wavelength. A variable concentration of an analyte present in cells, subcellular space, and the whole plant, for example, calcium and ROS, results in fast spatiotemporal pattern changes in waves with time and subcellular locations (Zhang et al., 2013; Kruss et al., 2014). Integration of different simulations, mainly diffusion and stochastic kinetic, helps to elucidate the complex data with a productive relationship under different resource deficiency and stress conditions. In the future, system biology integration of extensive biological data (affinities, the rate constant, sensitivity, selectivity, and dynamic range) via computational modeling that offers translation of plant chemical signaling into digital information is important for decision and action of agriculture devices.

In the past decades, wearable sensors have been developed through nanotechnological innovation for human clothing and skin application (Heikenfeld et al., 2018). Therefore, it opens a new window that offers wearable nanoelectronic circuits on plant surfaces for wireless communication of volatile compounds with low concentration in real-time. SWCNT channels and graphitic electrodes transferred onto leaf surfaces of live plants can sense trace levels of a gaseous compound down to 5 ppm concentration (Lee et al., 2014). Binding of SWCNT-based sensors equipped with copper complexes to ethylene gas emitted from plant fruits leads to changes in the resistance proportional to the volatile compound concentration (Esser et al., 2012). CNT-based senors are now available in the market for detection of ethylene, which is a plant hormone and crucial indicator of fruit ripping. Furthermore, plants embedded with functionalized SWCNTs with bombolitin peptide are used for real-time monitoring of explosive nitroaromatics (i.e., picric acid) in a smartphone or laboratory-grade camera for changes in nIR fluorescence intensity (Wong et al., 2017). Similarly, green fluorescent protein-based calcium sensors act as a detector for plant stress.

Nanobiotechnology-based sensors have the capacity for real-time monitoring of chemical signaling by phenotyping or agricultural devices embedded with smartphone, meteorological station, or hyperspectral imaging cameras to alleviate the environmental stress and selection of high yielder plant traits, for example, delivery of ZnO and cerium oxide NPs to protect the plant from heat and salinity (increasing potassium retention in leaf mesophyll) by scavenging reactive oxygen (Graham et al., 2016; Wu et al., 2017b, 2018). Similarly, CuO can protect from fungal root disease in watermelon (*Citrullus lanatus*), and nanocrystals reduce cold damage (Alhamid et al., 2018; Borgatta et al., 2018).

Smart plant sensors still need testing in agriculture field conditions, such as environmental condition, plant growth,

and how development can affect their performance. The communication of plant sensors with electronic devices is still limited to controlled laboratory conditions. If the field trials are fruitful, the sensor can provide real-time information regarding the requirement of nutrients, water, pesticides, and fertilizer for specific needs.

NPs FOR MANAGING THE AGRICULTURAL POST-HARVEST WASTE

Most of the recent literature on the application of nanotechnology emphasizes nano pesticides, nano fertilizers, nanosensors, and crop protection. The abundant amount of lignocellulose has been obtained from agricultural waste that can be utilized efficiently to prepare functional NMs, such as nanocellulose (Shahabi-Ghahafarrokhi et al., 2015), nanocomposites (Othman, 2014), and biochar. Rice and wheat husks can be used to produce value-added products that alleviate concerns about disposing of agricultural waste (Kaur et al., 2016). By utilizing electrospinning, waste cotton fibers and cellulose can be converted into value-added products (Ramakrishna et al., 2006). Cellulose is the most abundant biopolymer that makes the backbone of tree trunks and branches. It is also considered the main component of the paper industry. It can be efficiently utilized for the production and application of nanocellulose and natural fiber (Dai and Fan, 2013; **Figure 3**). Nanoscale cellulosic materials are very hydrophilic, called aerogels, that offer a wide range of applications. Their properties are very distinct from their bulk parts. Holocellulose aerogels can be widely utilized as adsorption materials owing to the nano-fibrillar structure with high surface area and high adsorbing properties (Muñoz-García et al., 2015). Silica, an inorganic element, can be extracted from the rice husk, which is known for its excellent source of nano and microsilica. The effective use of nano-silica conjugated with validamycin is for the controlled delivery of water-soluble pesticide (Liu F. et al., 2006). Nano silica conjugated with methyl methoxy silane was suggested as a plant growth regulator and nanofungicide against mildew disease (Huang et al., 2015). Some of the nano pesticides are already hitting the market (**Table 4**), but their relation to the controlled release of agrochemicals is still ongoing and may take several years. We reviewed the detailed information for NP-based companies' related products and properties (for more detail refer to **Table 4**).

TOXICOLOGICAL IMPACT OF NP RISK AND HEALTH HAZARDS IN AGRICULTURE APPLICATION

Despite huge research, limited progress has been made in understanding the NM risk and health hazards. NP application in agri-food industries majorly lacks the transparent and precise framework for risk governance across the different sectors (**Figure 1D**). The development of harmonized regulatory frameworks in the field of nanosafety has been focused on safety-by-design synthesis approaches (Kraegeloh et al.,

2018; Stone et al., 2018). To share the information among different nanotechnology, fields are required not only to show nanosafety research advancement, But also risk assessment, risk management, policymaking, and to support risk communication among the different stakeholders (for example, society, industries, researchers, policymakers, insurance companies, and the general public). Mostly, nanosafety researchers work with a two-way approach (Bos et al., 2015). The first approach is to understand human health toxicity, which is predominately targeted to organisms, tissues, and cells (for example, mouse skin and immune cells). Second is environmental health risk; communities are primarily concerned with other branches of the tree of life (for example, single-cell organisms, plant tissues, invertebrates, and fish). Subsequently, plant-based nanosafety research has been focused on the intentional or direct exposure of food crops to specific NMs (for example, nano pesticides, nano fertilizer, and nanoherbicides), indirect or unintentional exposure (i.e., spray drifting, leaching, and runoff of NPs; **Figure 5**).

The primary point that needs to be addressed before exploiting NPs in any field is their physiochemical properties as this could have a direct impact on their potential health and environmental hazards that somehow limit their actual potential as a beneficial entity. Of these characteristics, size and concentration are the foremost properties of the NPs important from the toxicology perspective (**Table 5**). It can be correlated with the increased surface area with a decreased size that ultimately leads to higher uptake and interaction with the plant system, thus increasing the chances of generating adverse effects (Nel et al., 2006). It has been extensively reviewed by Ma et al. (2010) that NPs of size <5 nm can readily be translocated through cell wall pores and 20 nm through plasmodesmata; thus, it can be perceived that NPs with lower size range can be quickly taken up by the plants and could cause more phytotoxicity even at lower concentrations (Ma et al., 2010; Rico et al., 2011; Wang et al., 2013). As in the case of larger size graphene oxide (GO), the potential translocation from roots to shoots is hindered, thus lowering the bioaccumulation (Chen et al., 2017).

It is worth mentioning here that the concentration-dependent effects also mark the critical evidence of NP benefits or toxicity. For instance, ZnO NPs and CeO$_2$ NPs show its toxic effects, such as reduced yield (31.6%), when supplied in higher concentrations (800 mg/kg) and not at lower concentrations (400 mg/kg) in cucumber plants (Zhao et al., 2013b). On the contrary, ZnO NPs promote seed germination and seedling vigor in addition to increased chlorophyll content when supplied in 1,000 ppm concentration to peanut plants (Prasad et al., 2012). The main mechanism of NPs toxicity is more specifically metal NPs relying on the formation of excessive ROS, particularly by shredding ions in the biological environment, thus creating toxic effects (Yan and Chen, 2019). It also interferes with the electron transport chain of mitochondria and chloroplast. Different stress factors also affect the carbon fixation that, in turn, causes photoinhibition and, ultimately, more production of superoxide anion radicals and H$_2$O (Foyer and Noctor, 2005). The resulting overproduced ROS further interacts with the cellular components, causing protein modifications, lipid peroxidation, and damage to DNA (Møller

TABLE 4 | List of commercial agricultural nano formulations based product companies, application with respective countries.

S.No	Company	Nanomaterial	Name of product	Properties	Application	Country
1.	Aqua-Yield Hub	Potassium (Nanocapsule)	NanoK™	• Crop Yield Enhancement • Potassium delivery to crops	Nano fertilizer	USA
2.		Zinc (Nanocapsule)	NanoZn™	• Plant Growth Regulation • Zinc delivery to crops	Nano fertilizer	USA
3.		Combined	NanoRise™	• Plant Growth Regulation • Plant Growth Regulation • Crop Yield Enhancement	Nano fertilizer	USA
4.			NanoPro™	• Plant Growth Regulation • Pesticide uptake enhancement and efficacy	Nano fertilizer	USA
5.	Silvertech Kimya Sanayi ve Ticaret Ltd.	Zinc oxide Titanium dioxide	NANO FERTILIZERS	• Plant Growth Acceleration • Crop Yield Enhancement • Photosynthesis Improvement • Soil salinization resistant	Nano fertilizer	TURKEY
6.	Land Green & Technology Co	Mn, Cu, Fe, Zn, Mo, N	NovaLand-F	• Preventing the growth of algae • Plant Growth Regulation • Plant Growth Acceleration • Increased resistance to plant diseases • Plant Metabolism Acceleration	Nano fertilizer	TAIWAN
7.			NovaLand Nano—Mn, Cu, Fe, Zn, Mo, N	• Head-heavy Balance • Plant Growth Regulation • Plant Growth Acceleration • Photosynthesis Improvement • Root Activity Improvement • Root Vigor Improvement Active • Growth Promoter Harvest enhancement • Soil salinization resistant	Nano fertilizer	TAIWAN
8.	Bio Nano Technology	NA	HYPER FEED 19-19-19	• Nutritional	Nano fertilizer	EGYPT
9.	NANOPAC (M) Sdn Bhd	NA	Nano fertilizer	• Antibacterial Activity • Non-toxic Environmentally Friendly • Antifungal Activity Plant Growth • Regulation Nutritional Plant Growth Acceleration	Nano fertilizer	MALAYSIA
10.	Microwell Bio Solutions Sdn Bhd	Potassium	Groagro 4: Super Kalium Catalyst + T.E	• Nutritional Value improvement • Plant Growth Acceleration	Nano fertilizer	MALAYSIA
11.		Potassium	Groagro 1: Super Nano-Catalyst Kalium + T.E	• Nutritional Value improvement • Plant Growth Acceleration	Nano fertilizer	MALAYSIA
12.	SHEPROS SDN. BHD.	NA	NANOSORB FERTILIZER BOOSTER	• Plant Growth Regulation • Nutritional Value improvement • Plant Growth Acceleration • Strengthening the supply of plant micronutrients iron and zinc and manganese • Plant Metabolism Acceleration	Nano fertilizer	MALAYSIA
12.	Bioteksa	Iron (Nanoparticle /Nanopowder) Magnesium (Nanocapsule)	NUBIOTEK® HYPER Fe+Mg	• Plant Growth Regulation • Nutritional Plant Growth Acceleration • Plant Resistance Enhancement	Nano fertilizer	Mexico

(Continued)

TABLE 4 | Continued

S.No	Company	Nanomaterial	Name of product	Properties	Application	Country
13.		Calcium (Nanoparticle /Nanopowder)	NUBIOTEK® ULTRA Ca	• Plant Growth Regulation • Nutritional Plant Growth Acceleration	Nano fertilizer	Mexico
14.	HPL Agronegocios	Magnesium (Nanocapsule)	FÉRTIL CALMAG	• Plant Growth Regulation • Absorption Enhancement	Nano fertilizer	Brazil
15.	Laboratórios Bio-Médicin	Manganese (Nanocapsule) Molybdenum (Nanocapsule) Zinc (Nanocapsule)	Nanovec TSS 80	• Agriculture Seed treatment	Nano fertilizer	Brazil
16.	HPL Agronegocios	Calcium Nanoparticle /Nanopowder	FERTILE CALCIUM 25	• Nutritional Absorption Enhancement	Nano fertilizer	Brazil
17.	Litho Plant	Calcium Nanoparticle /Nanopowder Manganese Nanoparticle /Nanopowder	Lithocal	• Nutritional Absorption Enhancement	Nano fertilizer	Brazil
18.	Samarita		NANOPOWER CaMag	• Plant Growth Acceleration • Crop Yield Enhancement	Nanofertilizer	Brazil
19.	Kimitec Group	Phosphorous (Nanoparticle /Nanopowder) Diameter : 2 nm Potassium (Nanoparticle /Nanopowder) Diameter : 2 nm	FOSVIT K30	• Self-defense enhancement	Nano fertilizer	Spain
20.	Tropical Agrosystem India (P) Ltd.	ZINC	TAG NANO ZINC	• Plant Growth Regulation • Photosynthesis Improvement • Root Activity Improvement	Nano fertilizer	India
21.		Calcium	TAG NANO CAL	• Plant Growth Regulation • Photosynthesis Improvement • Root Activity Improvement	Nano fertilizer	India
22.		POTASH	TAG NANO POTASH	• Plant Growth Regulation • Photosynthesis Improvement • Root Activity Improvement	Nano fertilizer	India
23.	Alert Biotech	Zinc (Nanoparticle /Nanopowder)	Nano Zinc (Chelated)	• PH stability • Nutritional	Nano fertilizer	India
24.		Boron (Nanoparticle /Nanopowder)	Nano Bor 20%	• PH stability • Nutritional	Nano fertilizer	India
25.		Zinc (Nanoparticle /Nanopowder)	Nano Zinc (Soil Application 21%)	• PH stability • Nutritional	Nano fertilizer	India
25.	Nano Agro Science Co-operative Society Ltd.	NA	Root Health	• Environmentally Friendly • Organic Root Activity Improvement • Root Vigor Improvement	Nano fertilizer	India
26.		Phosphorous (Nanoparticle /Nanopowder)	NASCO Escort-P	• Environmentally Friendly • Organic Root Activity Improvement • Root Vigor Improvement	Nano fertilizer	India

TABLE 5 | Detailed information on the toxicity of NP-based agrochemicals with various concentrations, size, and plant species tested.

S.No	Nanoparticles	Concentration	Size	Plant species	Effects	References
TOXICITY OF METAL AND METAL OXIDE NP-BASED AGROCHEMICALS						
1.	Fe_3O_4	30, 100, and 500 mg/L		*Lolium perenne* L. and *Cucurbita mixta* cv. white cushaw	Oxidative stress, increased superoxide dismutase and catalase enzyme activities, lipid peroxidation	Wang et al., 2011
2.	Citrate coated-Ag and ZnO	200 and 1,000 µg/mL, respectively	56.1 and 17.4 nm, respectively	*Zea mays* L. and *Brassica oleracea* var. *capitata* L.	Alterations in cellular structures, Tunneling effect with nZnO, metaxylem count changes by citrate coated Ag	Pokhrel and Dubey, 2013
3.	Ag	20, 51, and 73 nm	100 mg/L	*Vicia faba*	Altered PSII activity, stomatal conductance, and CO_2 assimilation,	Falco et al., 2020
4.	ZnO	5, 10, 25, 50, 75, 100, 125, 250, and 500 mg/L	<50 nm	*Brassica napus*	Inhibits root elongation at highest concentration (250 and 500 mg/L), effects on shoot elongation were less severe	Mousavi Kouhi et al., 2014
5.	ZnO	300, 600, and 1,000 mg /kg	<100 nm	*Solanum lycopersicum*	Increased APX and SOD activity levels, and lipid peroxidation in roots through generation of H_2O_2, altered contents of non-enzymatic antioxidants, total phenols, flavonoids, -carotene, and lycopene in fruits were significantly reduced	Akanbi-Gada et al., 2019
6.	Tio$_2$ and CeO	0, 250, 500, and 1,000 µg/mL	130–295 nm; TiO$_2$, 230–290 nm; CeO	*Lactuca sativa, Lycopersicon lycopersicum, Brassica oleracea, Glycine max, Daucus carota, Lolium perenne, Z. mays, Cucumis sativus, Avena sativa,* and *Allium cepa*	Plant species-dependent effects were observed, differential phytotoxicity depending on the nanoparticles type, significant changes in seed germination but no acute toxicity, lettuce, onion, ryegrass, tomato were shown effective for both the nanoparticles	Andersen et al., 2016
7.	CuO and Al$_2$O$_3$	0, 20, 200, and 2,000 µg/mL	18 nm; CuO and 21 nm; Al$_2$O$_3$	*Solanum lycopersicon*	ROS-mediated membrane damage and membrane lipid peroxidation is observed along with activity of antioxidant enzymes, DNA conformation by NPs is affected by both intercalative and non-intercalative modes, Al$_2$O$_3$-NPs induced lesser change in TmDNA conformation Macromolecular change in amide-I and II of proteins and carbohydrates, CuO with more toxicity than Al$_2$O$_3$, concentration dependent decrease in fresh and dry biomass	Ahmed et al., 2018
8.	CuO	0, 50, 100, 200, and 500 mg/kg	25, 50, and 250 nm	*Glycine max* cv. Kowsar	Particle size and concentration dependent toxicity, altered Antioxidant biomarkers with CuO NPs of 25 nm in soil	Yusefi-Tanha et al., 2020
9.	TiO$_2$ and ZnO	0, 5, 10, 20, 40, and 80 mg/kg	~30 nm	*Hordeum vulgare* L.	The antioxidant enzyme activities are diversely affected but no changes in seed germination and root elongation has been observed, ZnO was more toxic than TiO2	Dogaroglu and Köleli, 2017
10.	CuO	10, 50, 100, and 500 mg/L	20–40 nm	*Brassica oleracea* var. *botrytis* and *Solanum lycopersicum*	100 and 500 mg L^{-1} of CuO NPs has resulted in reduction of total chlorophyll and sugar content, augmented lipid peroxidation, electrolyte leakage, and antioxidant enzyme activity, concentration dependent increase in superoxide and hydrogen peroxide formation in leaves, deposition of lignin in roots seen at higher concentration	Singh et al., 2017

(Continued)

TABLE 5 | Continued

S.No	Nanoparticles	Concentration	Size	Plant species	Effects	References
11.	CuO	10 g/L	30–50 nm	*Hordeum sativum distichum*	Ultrastructural changes in chloroplast, vacuoles, mitochondria and stomata, impaired germination rate, root morphology, cell wall, epidermis, cortical layers and vascular bundles, Inhibits root, and shoot length	Rajput et al., 2018
12.	FeO	30, 40, or 50 mg/L	12 nm	*Lemna minor*	The chlorophyll content decreased at high iron oxide NP concentrations, which disrupted the light absorption mechanism, ROS production, diminishes photosynthetic pigments or chl a/chl b content ratio	Souza et al., 2019
13.	TiO_2, ZnO, Al_2O_3, and CuO	0.05, 0.5, 2, and 5 mg/ml	148–248 nm	*Raphanus sativus, Cucumis sativus, Solanum lycopersicon,* and *Medicago sativa*	Stimulates metallotheonein production, inhibited relative seed germination, root/shoot tolerance index however differential effects were observed based upon the plant species and nanoparticles type	Ahmed et al., 2019
14.	CuO, TiO_2, and Fe_2O_3			*Triticum aestivum*	Decreased contents of Fe and Zn by CuO treatment and reduced human essential amino acids, overall increased amino acid concentration by TiO_2,	Wang et al., 2019
15.	CuO, ZnO, and NiO	100, 250, 500, and 1,000 mg/L	25–55 nm; CuO, 18 nm; ZnO, 10–20 nm; NiO	*Abelmoschus esculentus*	Suppressed plant growth in a concentration-dependent manner, reduced shoot and root length, decreased chlorophyll content, significantly altered total phenolic and total flavonoid contents, enhanced ROS, and malondialdehyde production	Baskar et al., 2020
16.	Se	0, 0.5, 1, 10, and 30 mg/L	20 nm	*Capsicum annuum*	Impose epigenetic changes, upregulated bZIP1 and WRKY1 transcription factors, altered growth metabolism and anatomy of plant, caused DNA hyper-methylations	Sotoodehnia-Korani et al., 2020
17.	Se	0, 1, 4, 10, 30, and 50 mg/L	10–30 nm	*Momordica charantia*	More concentrations cause stem bending, impaired root meristem, and severe toxicity, cause variation in DNA cytosine methylation, reflecting the epigenetic modification, also stimulates activities of catalase and peroxidases, disrupts xylem conducting tissues	Rajaee Behbahani et al., 2020
18.	CeO2	0, 50, 100, and 1,000 mg	<25 nm	*Lactuca sativa*	Higher concentration treatment significantly deteriorate plant growth and biomass production, Superoxide dismutase, Peroxidase, Malondialdehyde activity was disrupted	Gui et al., 2015
TOXICITIES OF NANOTUBES (NT)						
19.	MWCNT and SWCNT	1 and 10 mg/kg	1–4 nm outer diameter and 5–30 μm length; SWCNT-OH, 30–50 nm outer diameter and 0.5–2.0 μm length; MWCNT-COOH	*Solanum lycopersicum*	Delay in early growth and flowering, MWCNT effects were seen on first fruit, SWCNT has effects on physiology, such as increased salicylic acid	Jordan et al., 2020
20.	Hollow MWCNT, Fe-filled carbon, and Fe-Co-filled carbon NT	0, 10, 50, and 300 mg/L	5 nm thickness	*Oryza sativa* L.	Inhibited rice growth, decreased concentrations of endogenous plant hormones, decreased nitrogen assimilation	Hao et al., 2016
21.	MWCNT	0, 125, 250, 500, and 1,000 μg/mL	Outer diameter 5–15 nm and length 50 μm	*Cucurbita pepo* L.	Toxicity effects on germination rates or slow germination of seeds, enhanced cellular injuries, inactivated antioxidant enzymes	Hatami, 2017
22.	MWCNT-COOH	0, 25, 50, and 100 mg/L		*Ocimum basilicum*	High dosage (100 mg L^{-1}) of MWCNTs-COOH leads to toxicity effects	Gohari et al., 2020

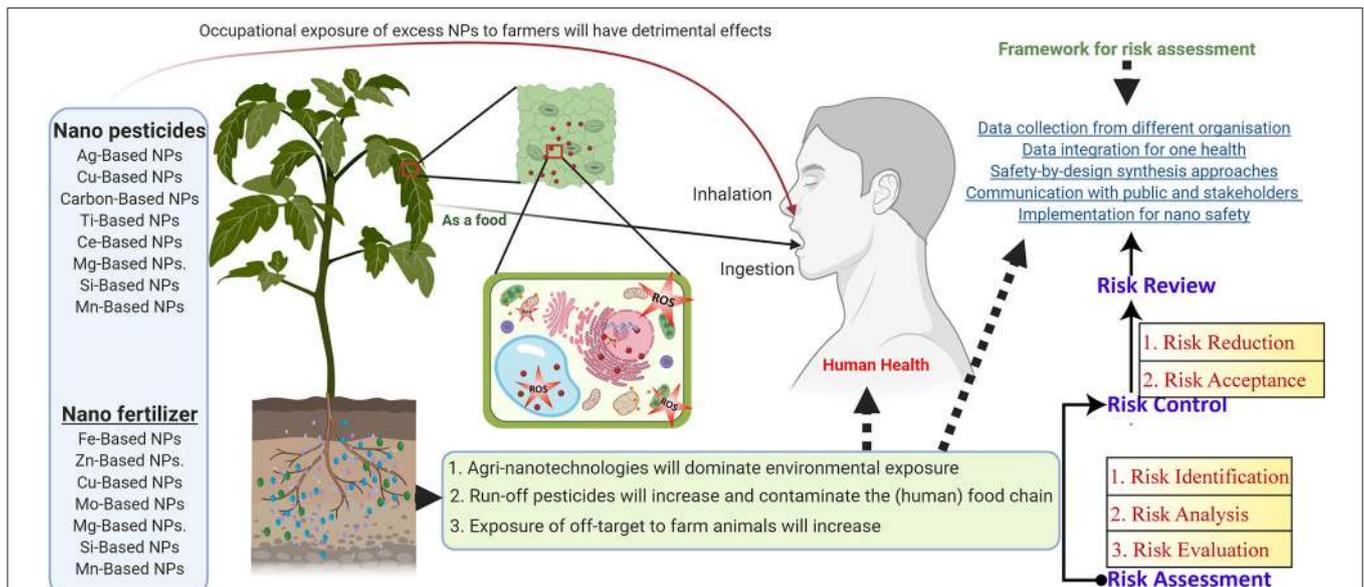*The summary of the results is also provided with specific reference citations.*

FIGURE 5 | Framework for the risk assessment of nanotechnology in the agri-food sector: The direct delivery of nano pesticides and nano fertilizers to plants can induce ROS, leading to intracellular organelles and function disruptions. Indirect release (i.e., released from agricultural products as well as food processing and packaging) results in the occupational exposure (i.e., from industrial processes, direct contact with nano pesticides and nano fertilizers) to humans. Risk framework for risk assessment, risk management, policymaking, and to support risk communication among the different stakeholders to improve agriculture nanotechnology sustainability.

et al., 2007, Huang et al., 2019, Wang et al., 2020). It also has positive implications as it helps in mitigating stress-related issues in plants that show the importance of equilibrium between ROS production and scavenging (Sharma et al., 2012). The increased ROS has substantial implications on the activity of antioxidative enzymes (also shown in **Table 5**) in plants under NP stress (Faisal et al., 2013; Jiang et al., 2014; da Costa and Sharma, 2016).

Recent reports have also shown that phytohormones play an essential role under external insult response signaling. The NPs cause a decrease in the auxins, cytokinins, and salicylic acid, suggesting hormone imbalance in plants, thus affecting overall metabolism (O'Brien and Benková, 2013; Vankova et al., 2017). A very high concentration of NPs may severely affect photosynthesis, which may result in plant growth suppression or plant death. Several reports have observed significant decrease or inhibition in plant growth as the result of NP exposure (for more detail refer to **Table 5**).

In light of the reports mentioned above, it can be perceived that several factors come into the picture that have to be considered before realizing the positive utilization of NPs in the agricultural system. Plant–soil interaction is the main driving force for agricultural production; thus, it is critical to study the physicochemical characteristics of the soil system. It is considered to be the paramount sink for the NPs, and hence, their interaction with the soil components could impose a profound impact on the fate of NPs. It has been observed that pH, organic content, and cation exchange capacity results in an increased risk of toxicity (Servin and White, 2016). For instance, loamy clay soil with pH 5.5 reported no toxicity by ZnO NPs even at a concentration of

2,000 mg/kg, whereas, loamy clay soil with pH 7.36 observed noticeable toxicity at a concentration of 45.45 mg/kg (Du et al., 2011). In addition to this, the soil organic matter also plays a significant role in changing the safety issues of the NPs as evident from reduced toxicity of the ZnO NPs when provided with Alginate at a concentration of 400–800 mg/kg. However, ZnO NPs alone cause a significant reduction in plant biomass (Zhao et al., 2013a). NPs also have a direct impact on the soil microbial community structure in a dose-dependent manner as observed by using DNA fingerprinting analysis that showed declining taxa of Rhizobiales, Bradyrhizobiaceae, and Bradyrhizobium (nitrogen fixation process); however, positive effects were also envisaged on Sphingomonadaceae and Streptomycetaceae. It is interesting to note here that NPs are declining the taxa related to nitrogen fixation while increasing the taxa of the community associated with the decomposition process of organic pollutants and biopolymers (Ge et al., 2012). Furthermore, AgNPs showed a dose-dependent impact on the nitrate-reduction activity of Rhizobium and Azotobacter with a 0.2 ppm increase in the activity in Azotobacter (Shahrokh et al., 2014). Environmentally based nanosafety research has primarily targeted accidental environmental releases of NPs during the manufacturing, use, and disposal of nanoformulized agriculture nanoproducts. Mukherjee et al. (2016) studied the comparative toxicity of NPs Al_2O_2 at ZnO (15 nm), ZnO at $KH_{55}0$ (20 nm), and bare-ZnO (10 nm) to grown green peas (*Pisum sativum* L.) (**Figure 5**). Plants treated with Al_2O_3 at ZnO NP (1,000 mg/kg for 65 days) had higher Zn level in seeds and roots relative to bulk and the other Zn NP exposure. Photosynthetic pigments (Chl-*a* and

carotenoid) significantly increased, but the carbohydrate and protein content remained largely unaffected across all treatments except Al_2O_3 at ZnO NP. In correspondence, a very high concentration of ZnO NPs (1,000 mg/L) did not significantly alter root elongation and seed germination. In contrast, Cu and Ag-NPs inhibited root growth of zucchini (*Cucurbita pepo*). The exposure of AgNPs at a concentration of 500 and 100 mg/L resulted in 57% and 41% drastic reduction in plant biomass and transpiration rate, respectively (Stampoulis et al., 2009).

Wang et al. investigated the impact of 200 and 300 (mg/L) ZnO NP exposure, which decreased *Arabidopsis* growth by ~20 and 80%, respectively, relative to the control. The results show a decrease in the expression of chlorophyll synthesis genes and photosystem structure genes. In contrast, an increase in the expression of carotenoid synthesis genes may contribute to reducing the photosynthesis efficiency linked to overall phytotoxicity in the plants. Asli and Neumann (2009) report that colloidal suspensions of TiO_2-NPs (30 nm) accumulated in the root at the cell wall surfaces and decreased cell wall pore size from 6.6 nm to about 3 nm, affecting water transport capacity and, therefore, transpiration of intake plants (*Zea mays* L.). Genotoxic and phytotoxic impact of CeO_2 and TiO_2 NP suspensions were investigated on the early growth of barley with concentrations of 0, 500, 1,000, and 2,000 mg /L for 7 days (Mattiello et al., 2015). Genotoxicity [randomly amplified polymorphism DNA (RAPDs) and mitotic index] observed changes in RAPD banding patterns and the chromosomal level with decreasing cell divisions in treated root tip cells compared to control plants. ROS generation and ATP content increased at the concentration of 500 mg/L in both root and shoot (**Figure 1D**). Authors also observed the presence of CeO_2 and TiO_2 NPs in exposed root cells through ICP-OES and TEM EDSX microanalysis.

Indeed, theoretically, there may be the direct release of NMs into the environment from agro-nanotechnologies and incorporation into the human exposure pathway through the food chain. The existing challenges facing agricultural nano chemical application are due to the potential migration of NMs through the food chain, so safety assessment is urgently required. There are various modes of exposure of nanoagrochemicals to humans, such as growing demand for food crops (for example, population growth and increasing demand for animal-based products), large food product waste in affluent industries, and other agriculture activities (pre- and post-harvesting of food crops) (**Figure 5**). In addition, plants present a significant opportunity to facilitate the transfer of NPs to the different tropic levels and ultimately to the food web as they are largely consumed by the lower trophic-level organisms, animals, and people.

It is important to understand the one health concept, especially in the context of agriculture nanotechnology. One cannot minimize the previous research or reports focusing on the need for viewing of modern challenges to health through a one health concept; this cannot be underestimated. Also, many peer-reviewed articles frame their research finding as an example of the demand for a one health approach. We must also appreciate the excellent effort of various international organizations (World Health Organization, the World Organization for Animal Health, and the Food and Agriculture Organization of the United Nations) devoted to promoting the one health concept and spreading the awareness of their importance (Lombi et al., 2019). Here, we propose a transdisciplinary and holistic approach that underpins the one health concept and is crucial for sustainable development and policy implementation of nanotechnology (**Figure 5**). We are living in an interdependent ecosystem wherein all the organisms on the planet, including humans, animals, plants, and associated microbiota, stay together for their existence by mutual interaction. In particular, the overuse and inappropriate practices of agrochemicals as growth promoters of food crops significantly increase the migration of NMs in the food chain. The nanotoxicity and associated human health hazards require an intelligent testing strategy framework for risk evaluation of agro-nanotechnologies. Along with preliminary assessment (document) of the existing knowledge and the gaps, they categorize and integrate data to develop an intelligent approach to grouping NMs based their properties (for example, particle size, charge, molecular weight, solubility, and composition) and their biological impacts in order to intelligently design next-generation risk-assessment strategies and safety to the risks emerging from this technology.

FUTURE PERSPECTIVE

Nanotechnology strikes at an indispensable part of numerous domains of the food industry without any doubt. It has promising applications; however, it cannot be overlooked that most of the knowledge we gathered about it is mainly from laboratory experiments. It is almost uncertain about apprehending the practical application while not understanding its impact on environment-related toxicity. Furthermore, not having the guidelines, regulatory bodies, and similar organizations creates obstructions for the selling of novel NP-based agrochemicals. Hence, there is a requirement to execute large trials in forwarding and developing futuristic investigations based on perceived gaps of knowledge. In this setting, we propose six critically important fundamental features:

1. The open government awareness program to educate the common people about food nanotechnology and its applications through formulating an adequate database and proof to assist as logistic support of both the public and food manufacturers.
2. The comprehensive examination of future studies must be featured to determine the risk associated with the usage of NP-based products in the agricultural sector to make a more practical strategy.
3. To identify the minimum concentration dose utilizing the concentration-dependent study in the natural soil system for the NP, which would be non-toxic and can be useful in field applications.
4. To gain a comprehensive understanding of the bioaccumulation capability of NPs during field applications and its effect on nanotoxicity and further knowledge of tropic chain transfer in the ecosystem chain and deciphering the sufficient safety estimate.
5. Broad understanding of soil physico-chemical interaction with NPs for reducing danger toward not distorting the soil microbiota. Further determination of the rotation of soil for

modifying the destiny, carrier, and bioavailability of NPs to diminish their following toxicity and their trustworthy and useful utilization in agriculture.

6. Last, we strongly suggest the substitution of synthetic NPs to biosynthesized and performing in-depth research. In this way, utilizing the environmentally friendly protocol may hold comparatively minor or no toxicity, and henceforth, future studies must specifically concentrate on their functional efficiency. In addition, pilot studies must be set in natural conditions (growing plants in soil) to give an explicit depiction of the environmental influence of NPs.

In Addition, Some Safety Measures Should Be Considered

1. It is crucial to harmonize the frameworks of nanosafety regulations focusing on safety-by-design synthesis approaches so that it should not be overused at the toxic level.

2. The physiochemical properties of any new NP-based agrochemical should be analyzed substantially in long-term experiments before exploitation in any field work as it could have a direct impact on health and environmental hazard that will limit the actual potential as a beneficial entity.

3. Environmentally based nanosafety research has to be primarily targeted to study the accidental environmental releases of NPs during the manufacturing, use, and disposal of nanoformulized agriculture nanoproducts.

CONCLUSION

The present review highlights the different roles of NPs in the agriculture and livestock industry. The implementation of nanotechnology in modern agriculture helps in uplifting the global economy by providing support and advances in different ways. Considering different challenges posed by the increasing population, plant diseases, animal diseases, and climate change, the introduction of NPs significantly contributes to addressing these pressing issues, expanding the use of conventional pesticides and fertilizers to enhance crop production, ultimately

causing harm to the natural environment. With the advent of NPs the effectiveness and agronomic efficiency are highly improved compared to traditional resources. The better use of pesticides encapsulated in different nanoformulations provides their better application, and controlled release protects the environment. Several nano pesticides and nano fertilizers are under development, and a few of them are already marketed. The study of NP–plant interaction is an important point to consider to understand the physiological and biochemical responses imposed by plants. Emerging techniques are developed to locate and quantify NPs through the plant system that gives the idea of their transformation and safety aspects in a complex system. Nanotechnology exploits the unique property of NPs and develops nanosensors to detect pesticide residue and various soil parameters, such as pH and moisture.

CONSENT FOR PUBLICATION

The authors gave their consent for publication of the research results.

AUTHOR CONTRIBUTIONS

DM, GK, and SA designed and wrote the manuscript. DM, GK, PS, KY, and SA revised and finalized the draft. SA supervised the whole project and reviewed the manuscript. All authors contributed to the article and approved the submitted version.

ACKNOWLEDGMENTS

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