Review Article

The Impact of Various Nanomaterials and Nano-Agrochemicals on Agricultural Systems

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ABSTRACT

Agriculture has always been one of the most important and stable parts of human life for thousands of years because agricultural activities produce and supply raw materials for the food industry and animal feed. With the rapid increase of the population on the planet, besides the need to increase agricultural production, mankind will face many limitations in the supply of resources such as land, water, soil, etc. Although various fertilizers and pesticides have been very beneficial in increasing the production of agricultural products, their residues in soil and water cause damage to the environment, vegetation, and living organisms. The use of various nano-based technologies in agriculture (for example, in the design of nano-fertilizers/nano-pesticides with controlled release, nano-sensors, nano-fuels, nano-based soil conditioners, water treatment systems, gene transfer to plants, etc.) can increase agricultural production and save costs reduce environmental risks due to the controllable amount of agrochemical release, the right time, and the target area of agrochemicals. Nanotechnology can be further used to detect diseases in a rapid manner, improve the ability of plants to absorb nutrients from the soil, enhance food quality and safety, and reduce agricultural inputs. However, the use of nanotechnology in agriculture is still in the early developmental stage, and more research is needed to understand the potential risks of nanomaterials. Nano-enhanced products should undergo the same thorough approval processes as conventional pesticides and fertilizers. In addition, it is crucial to exercise caution in their use to minimize the release into groundwater.

Introduction

Agriculture has always been one of the most important and stable parts of human life for thousands of years, because agricultural activities produce and supply raw materials for the food and feed industries. With the rapid increase of population on the planet, human beings will face many limitations in the supply of resources such as land, water, and soil [1]. In the present era, with the human movement towards the use

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of new technologies, the issues related to the use of nanotechnology have a special place in the field of modernization and updating of old technologies. On the other hand, the successful application of various models related to nanotechnology in medicine and in laboratory conditions has created many incentives to use the nanotechnology industry in agriculture. New technologies have made possible the controlled release of minerals or chemicals needed in agriculture. The utilization of biodegradable materials for nanoencapsulation of chemicals facilitates the safe and efficient delivery of essential active ingredients to plants [2]. Excessive and unnecessary use of chemical fertilizers, pesticides, and other agrochemicals in the last century has caused great damage to the environment and endangered the survival of human life and species on this planet. The pursuit of integrating nanotechnology into agriculture will persist, as conventional agricultural methods are limited in their ability to surpass current levels of productivity and restore ecosystems damaged by existing technologies to their original state [3].

Nanotechnology represents a novel field of study that encompasses various technologies involving structures and processes at the nanometer scale. Nanoparticles exhibit notable properties distinct from their bulk counterparts. Typically ranging in size from 1 to 100 nanometers in at least one dimension, nanoparticles or nanomaterials can be categorized into two groups: organic and inorganic [4]. The history of nanoscience and nanotechnology is intricate and diverse, tracing its origins across various disciplines such as physics, chemistry, and biology. The term "nanotechnology" was initially coined by physicist Richard Feynman during a 1959 talk entitled: "There is Plenty of Room at the Bottom", where he discussed the potential manipulation and control of individual atoms and molecules. Nevertheless, the utilization of natural nanomaterials by early humans dates back to prehistoric times. It can be asserted that nature itself served as the original nanotechnology engineer, evident in the formation of nano-droplets in nature. These droplets play a crucial role in climate change, the microphysics of clouds, the survival mechanisms of animals in cold environments, and a wide array of technologies [5]. In the eras of both industry and post-industry, and within the electrical sector, the concept of size reduction is not a recent development. Classical Japanese literature from the tenth century, for instance, lauds smallness as a form of beauty. Traces of nanostructured materials also emerge from antiquities spanning various historical periods, including the Middle Ages. During this time, medieval glassmakers can be regarded as pioneers in nanotechnology. Investigations reveal the use of gold nanoparticles in the exquisite glasswork found in churches of that era. Notably, these artisans were unaware of the scientific reasons behind the color changes induced by adding gold to glass. Another renowned example is the Lycurgus Cup in Rome, dating back to the fourth century AD [6]. While the cup appears green in daylight, it transforms into red and pink when illuminated. This captivating optical phenomenon is attributed to the incorporation of gold and silver nanoparticles (Figure 1).

Figure 1. Lycurgus Cup [7]. The glass appears either green (A) or red (B) depending on the direction of the light source, owing to minute particles of gold and silver added to the glass

In 1986, K. Eric Drexler introduced and redefined the term nanotechnology in his book "Engines of Creation: The Coming Era of Nanotechnology" [8]. He explored the term in more depth in his doctoral dissertation and later developed it in a book entitled "Nanosystems: Molecular Machinery, Manufacturing, and Computation". In fact, Drexler was the founder of molecular nanotechnology. He was a student of Minsky, the father of artificial intelligence, who brought together a group of computer students as a community. Based on Feynman's ideas, they pursued what he called nanotechnology. Drexler's research showed chemists how the science of molecules and the bonds between them could serve as the basis for the further development of instrument-making systems in nanotechnology. He also showed engineers and physicists how to reduce macromolecular systems to molecular scales [9].

Regarding the application of nanotechnology in agriculture, there are several reasons to justify its use. Excessive and unnecessary use of nitrogen, phosphate fertilizers, and pesticides has been shown to increase eutrophication and toxins in groundwater and surface water. This in turn can increase the growth of cyanobacteria and algae as well as the toxins production in water contaminated with these substances, creating many environmental hazards for aquatic and terrestrial organisms. In addition, excessive use of these agrochemicals not only damages the soil and its microflora, reduces vegetation and soil erosion, but also causes economic problems for the agricultural industry due to rising prices of mineral and chemical products [3].

Nowadays, nanotechnology may potentially be used in agricultural systems such as agricultural machinery (increasing resistance of tools to abrasion, corrosion and dust), nanofuels, nano-based soil conditioners, pesticide and fertilizer production, water treatment systems, and gene transfer to plants and animals [10], Biomass [11], increase plant resistance to disease [12], gene upregulate and downregulate as well as modulate plant relationships with environmental microorganisms [13].

Nanotechnology in agriculture

The importance of nanotechnology in agriculture

As time goes on, the benefits of nanotechnology, especially in the field of agriculture, become more apparent [14]. While the significance of nanotechnology applications in agriculture has gained attention only in recent years, research in this field commenced approximately half a century ago. In the nanoscale realm, materials typically display unique properties not observed in their bulk counterparts. At this scale, the surface area, cation exchange capacity, ion adsorption, complexation, and various other functions of clay are greatly amplified. A notable distinction between nanoparticles and bulk materials lies in the significantly higher proportion of atoms on the nanoparticle surface compared to macro-sized particles. Nanoparticles can exhibit varied surface compositions, densities, and reactivities, stemming from processes like adsorption and redox reactions. These characteristics can be harnessed beneficially in the creation of nanomaterials for agricultural purposes [3]. Increasing the production and exploitation of agricultural products through cultivation improvement, crop management, and protection against pests and diseases, has been essential among farmers from the past to the present. Today, despite the new technologies and conventional technologies in the agricultural sector, there are many problems in agriculture. Nanotechnology is the knowledge of using very small particles that solve problems in the agricultural sector. In addition to the above-mentioned points, nanomaterials can be used in agriculture today to increase fertilizer use efficiency, increase yield and reduce the need for pesticides, rapid detection of pathogens, detection of toxic chemicals in food, and regulate agricultural food security. Therefore, today we must accept the fact that nanotechnology can be used as a set of new and advanced techniques in the service of the agricultural system to increase crop production. For example, nano-filters or nano-catalysts can degrade existing pollutants and ultimately reduce pollution. Nanotechnology can be further used to produce slow-release nano-fertilizers for plant nutrition or to produce nano-pesticides or nano-capsules containing pesticides for controlled release as needed, which in turn can improve crop growth. Utilizing this technology in agriculture extends to delivering site-specific drugs and nutrients in fisheries and livestock, employing nano-membranes for water and soil treatment, conducting cleaning and maintenance in fish ponds, and deploying nano-sensors for evaluating plant health and soil quality [15]. All of these can help to correct traditional farming methods and lead to healthier and more productive production. Phosphorus (P) is a natural element that plays an important role in agricultural production and plant health, but on the other hand, the use of phosphorus fertilizers has exacerbated the problem of eutrophication in surface waters and lakes. Studies have shown that synthetic phosphorus nanoparticles (apatite) may be able to provide sufficient phosphorus for agricultural products, but with less mobility in the environment and with less biological phosphorus for algae compared to soluble counterparts. Therefore, the nanofertilizers utilization for precision nutrient release can be seen as an effective approach to reduce the infiltration of phosphorus substances into both groundwater and surface water [16].

Some roles of nanotechnology in modern agriculture

To sum up, if we want to describe some applications of nanotechnology in agriculture, we must mention the following:

Precision agriculture

Precision Agriculture is a new perspective on the management of cultivated areas. With the help of nano-sensors, it is determined how much nutrients and nutrients are needed in each part of the agricultural land and the amount of soil toxins and environmental pollution is measured and with accurate control and timely reporting of plant needs to the system information processing center [17,18].

Reduce the use of herbicides and pesticides

Over the past years, nanoparticles have been used to produce a variety of pesticides such as insecticides, acaricides, fungicides, nematicides, bactericides, herbicides, etc. In most of the mentioned cases, nanoparticles have been used for production and transportation of agrochemicals in such a way that the effective substance of pesticides is gradually released and in addition to be cost-effective, it causes environmental safety, prevents soil erosion, reduces plant damage, and reduces toxicity to humans [19,20].

Application of nanotechnology in irrigation of agricultural fields/ reduce pollution and wastewater

Nanotechnology has the potential to increase the resistance of plants to diseases and pests, and advances in nanotechnology have led to changes in the behavior of plant cells, allowing them to grow with increasing longevity and rapid growth in adverse environments, even in salt marshes or water shortages, and increasing resistance to cold and drought conditions. With the help of this technology, food production companies are developing new nanomaterials that increase the length of time food stays healthy. Nanotechnology is positioned to instigate fundamental transformations in the utilization of natural resources, energy, and water, resulting in a reduction of both wastewater and pollution. Therefore, with the help of these new technologies, it has become possible to remove and reduce pollution with a very small diameter from water and air sources. The possibility of recycling and reusing materials, energy, and water is one of the main concerns of today's societies. The use of nanotechnology for water treatment and desalination of surface and groundwater can lead to greater protection of nature and environmental safety [21].

Increase the therapeutic power of drugs for livestock

This technology creates the ability to create new formulations and ways to deliver drugs that effectively increase the therapeutic power of drugs for livestock. For example, efforts were being made by nanoparticles to combat coronavirus in animals [22].

Biodegradable and compatible nano-pesticides

In all countries, most pesticides are synthesized and produced with the aim of pest control in the agricultural sector. The application of these pesticides and their usage contributes to environmental pollution. With the help of nanotechnology and the creation of new formulations for pesticides, it will increase the performance and reduce the consumption of pesticides. In the next section, we will provide detailed information about nano-fertilizers [23].

Nanotechnology interventions in agriculture

Water treatment

The impact of nanotechnology on numerous scientific and technical domains, particularly environmental safety, is growing steadily. A crucial application of nanotechnology in the environmental context is seen in water and wastewater treatment. Here, diverse nanomaterials employ adsorption, separation processes, and various other methods to effectively eliminate contaminants, pathogens, and other hazardous elements. Therefore, using nanotechnology, different nanoparticles are used to purify drinking water or agricultural water, which in turn controls diseases and regulates plant growth and increases crop production [24]. Identifying contaminants such as heavy metals is important to monitor proper plant growth. The utilization of magnetic metal/metal oxide nanocomposites provides an efficient means to separate heavy metals through a magnetic field. For instance, multi-walled carbon nanotubes (MWCNTs) combined with ferrous ferric oxide (Fe_3O_4), denoted as MWCNT/nano-Fe_3O_4, exhibit a higher adsorption capacity for Chromium (Cr^{3+}) in aqueous solutions compared to pristine MWCNT or activated carbon. Similarly, alumina (Al_2O_3) multilayer carbon nanotube nanocomposites (MWCNT/Al_2O_3) demonstrate excellent capability for Pb^{2+}. Another notable metal oxide, titanium dioxide (TiO_2), proves highly effective in nanocomposites for detecting and removing heavy metals. TiO_2 achieves the removal of various heavy metals through surface complexation mechanisms, while graphite oxide (GO) accomplishes heavy metal removal via electrostatic interaction. The formation of flower-like structures based on TiO_2 on GO nano-sheets enhances the removal of heavy metals such as cadmium, lead, and zinc. Given that toxic heavy metals are typically not present in elemental forms, the use of carbon-based nanomaterials proves highly effective in adsorbing these toxic forms. Moreover, iron oxide nanotubes and nanosheets have demonstrated effectiveness in removing arsenate and arsenite by utilizing positively charged iron particles for electrostatic interaction. In addition, magnetic graphene oxide, with a high loading of iron oxide, has proven effective in the removal of arsenate and arsenite [25,26]. Research has explored the *in vitro* application of zero-valent iron nanoparticles (nZVI) to compost derived from organic waste, aiming for soil decontamination [27]. The stabilization of metals with nZVI can impede their migration to groundwater across diverse soil layers. The effectiveness of nZVI-treated soils in stabilizing lead and zinc has been evidenced through leachate analysis [28]. Numerous studies have underscored the utilization of nanoparticles derived from noble metals, including Ruthenium, Rhodium, Palladium, Silver, Osmium, Iridium, Platinum, and Gold, in water treatment. Gold (Au) and silver (Ag) nanoparticles, in particular, are frequently employed for the detection of low levels of organic pollutants due to their distinctive visual properties. Noble metal nanoparticles have also demonstrated efficacy in the photocatalytic degradation of various water contaminants such as dyes, halogenated organics, and pesticides. An illustrative example is the use of TiO_2 doped with noble metal catalysts for the photocatalytic degradation of organic water pollutants. In addition, a range of electrodes incorporating bimetallic nanoparticles (such as Au/Pt, Ag/Au, or Ag/Pt) has been investigated for sensing, monitoring, and photocatalytic detection of contaminants [24]. Apart from the contamination detection, the inactivation of bacteria and pollutants can be mentioned as other advantages of noble metal nanoparticles. Several nanocomposites based on noble metals have been produced, some of which include Ag/ZnO, Pt/ZnO, and Ag/AgBr/graphene oxide nanocomposites. In the case of catalytic energies, several nano-catalysts based on platinum, lead and silver can be used. Gold nanoparticles have also been used to absorb Ag from water. The biocidal capacity of silver nanoparticles as a water disinfectant has been investigated. These nanoparticles may be used to control aquatic microorganisms such as Escherichia coli. It has been suggested that silver nanoparticles directly cause disruption in the cell membrane through binding. Likewise, these nanoparticles probably improve the antibacterial effect by increasing the atomic density and changing the shape of the nanoparticle or changing the crystal structure of anti-bacterials [29]. TiO_2 nanoparticles are more capable of absorbing Ni (II), Pb (II), Cd (II), Cu (II), and Zn (II) (329.8 nm). Larger pore size and crystallinity of TiO_2 nanoparticles may further alter the adsorption capacity. As mentioned earlier, silicon dioxide nanocomposites are another metal oxide used to purify and disinfect water. Due to its easy synthesis, environmental compatibility, specific surface area or SSA (50-500 nm) and low cost, SiO_2 has become a common nanoparticle in this field. Dithiocarbamates containing SiO_2 nanoparticles were further used to adsorb a range of mineral metal contaminants by multi-channel affinity and different factorization methods [30].

Nano-sensors in agriculture

Another benefit of nanotechnology in agriculture is the synthesis and application of nano-sensors/ nanobiosensors to increase production of crops. Nano-sensors can generally be useful in Precision Agriculture. Nano biosensors in the food and agricultural industry are efficient and cost-effective. In addition to detecting heavy metal ions, pollutants, and control of diseases and micro-climate around the plant, these nano-sensors can be used to identify pests and weeds, resulting in the proper use of pesticides [31]. In the realm of food packaging, the distinctive chemical and electro-optical properties of nano-sensors offer a means to address the drawbacks associated with traditional packaging. These nano-sensors have the capability to identify the presence of gases, aromas, chemical pollutants, pathogenic agents, and even fluctuations in environmental conditions [32]. Nano-sensors can be made of different materials. One of the non-metallic materials used in making nano-sensors is carbon. Carbon nanotubes are nanomaterials used to store energy and help in filtration, and in agriculture, they help to increase growth and transfer nutrients from the soil to plants. Chemical sensors based on carbon nanomaterials have been developed to detect pesticide residues in plants [33,34]. Metal nanoparticles such as gold (Au), platinum (Pt), and palladium (Pd) have become an important component in sensor transducers due to their potential and high sensitivity. Nanoparticles of noble metals can resist oxidation even at high temperatures due to their strength against corrosion. Gold nanoparticles play a role in sensors due to their unique properties. Colloidal gold (gold nanoparticles with sizes between 1 and 100 nm) has been investigated in the production of sensors. Gold-based electrodes, used in nano-sensors, enable the transfer of electrons between biomolecules and the transducer. Silver nanoparticles under controlled sizes can be used to detect Hg (II) ions [35]. Fluorescent nanoprobes synthesized from silica nanoparticles (conjugated with goat anti-rabbit secondary antibody) have been used to detect the plant pathogenic bacterium *Xanthomonas axonopdis* (the cause of bacterial spot disease in solanaceous plants). Tris-2, 2′-bipyridyl dichloro ruthenium hexa hydrate dye is further used on the core surface of silica nanoparticles that produce fluorescence [36]. Regarding plant diseases, it can be mentioned that nanosensors will play an important role in the present and future. Plant pathogens cause a lot of damage to plant products every year. For example, they reduce the global production of food grains by 14%, and under favorable conditions, some pathogens can cause the complete destruction of crops or fruits, so plant diseases can threaten food security in the world. The Ug99 race of black rust pathogen of wheat (*Puccinia graminis* f. sp. *tritici*) has migrated from Kenya and Ethiopia to other countries since 1999 and has been reported from different regions of Africa and neighboring countries of the Middle East [37]. The Ug99 strain is estimated to cause 10% yield losses in Asia, which is approximately $1-2 billion per year [38]. In addition, wheat stripe rust (*Puccinia striiformis* f. sp. *tritici*) and wheat leaf rust (*Puccinia triticina*), rice blast (*Magnaporthe oryzae*), and other fungal, bacterial, and viral diseases all over the world annually cause great losses in cereal crops (wheat, barley, rice, etc.) It has been stated that diseases and pests in some plants cause annual damage of 38 and 26% primary and secondary in foliage, respectively [39]. The combined invasion of pests and diseases can cause 82 and 50% reduction of achievable yield in cotton and food grain crops, respectively [40]. Therefore, monitoring dangerous diseases and pests using nanosensors as well as satellite information can be very useful for increasing the healthy production of products. Evidence suggests that the integration of nanobiosensors with biomarkers enables the extraction of rapid, precise, and accurate information concerning early infection and disease progression in real-world conditions. Nanosensors can be categorized according to their detection purposes, constituent materials, and the signals employed for information transmission. Recent reports highlight the practical application of nanosensors as an excellent tool for enhancing the sustainability and safety of crop cultivation. This is achieved by minimizing the consumption of agrochemicals necessary for maintaining crop growth and health [41].

Different types of nanoparticles can also be used as a sensing agent to detect different types of bacterial, fungal, and viral diseases. Nanoparticles can be used directly for pathogen detection or they can identify indicator compounds that play a role in disease progression. For example, gold nanorods functionalized with antibodies have been used for rapid detection of viral infections caused by *Odontoglossum ringspot virus* (ORSV) and *Cymbidium mosaic virus* (CymMV) in ornamental crops. The limit of detection (LOD) values for ORSV and CymMV infections in orchid leaves were found to be 48 and 42 pico gram ml^{-1} [40]. Also, an immunosensor based on gold nanoparticles has been developed to confirm Karnal bunt (*Tilletia indica*) contamination in wheat using SPR (Surface Plasmon Resonance) technique [42]. As mentioned previously, some researchers have synthesized fluorescent silica nanoparticle in combination with specific antigen of *Xanthomonas axonopodis* pv *vesicatoria* to confirm bacterial spot disease in *solanaceae* [36]. To identify the presence of the Sclerotinia sclerotiorum fungus in oilseeds, researchers have developed an electrochemical sensor comprising a gold electrode modified with copper (Cu) nanoparticles. Experimental results indicate that gold electrodes modified with copper nanoparticles can function as salicylic acid (SA) sensors, showcasing a significant enhancement in the electrochemical behavior of SA. To evaluate *Botrytis cinerea* contamination in apple, grape, and pear fruits carbon-based screen-printed electrode using microfluidics principles has been investigated. The results have shown that with this method, the examination time is reduced and the accuracy of diagnosis is increased [43]. To confirm the presence of Cucumber Mosaic Virus (CMV) with a detection limit of 10 ng/ml, the lithography patterned nanowire electrode (LPNE) deposition technique has been studied using a chemical resistance sensor modified with polypyrrole (PPy) nanoribbons [44]. In another study, a sensor based on nanoparticles and copper oxide nanolayer (CuO) was designed to detect *Aspergillus niger* in food. In this study, sol-gel and spray pyrolysis techniques have been used to develop CuO nanoparticles and nanolayers, and the principle of electrical resistance has been used to measure the bio-sensory properties of the developed nanostructure [45]. Certain scientists have employed bio-labeling coupled with immunomagnetic separation to achieve swift and precise detection of plant viruses. Magnetic nanoparticles (MNPs), sized at 100 nm, were coated with diverse antibodies and utilized as signal probes for the identification of Tomato Ring Spotted Virus (ToRSV), Bean Pod Mottled Virus (BPMV), and Arabis Mosaic Virus (ArMV). The key advantages of this assay include simultaneous detection of multiple distinct organic fluorophores, mitigation of non-specific virus absorption, a low fluorescent background, and high sensitivity and selectivity in targeting the viruses of interest [46]. In addition to the mentioned cases, the synthesis and application of nanoparticles derived from semi-conducting metal oxide have been studied for the detection of volatile organic compounds (VOC). For example, SnO_2 and TiO_2 nanoparticles have been reported to detect the chemical p-ethylguaiacol released by the strawberry fungus *Phytophthora cactorum* and other compounds of pathogenic origin [47]. Finally, it can be mentioned that the use of nanosensors in agriculture by controlling and providing diagnostic tools for the early diagnosis of plant diseases has brought many hopes for the management of viral, fungal, bacterial, and other plant pathogens. Important features such as speed and accuracy for diagnosing diseases in the early stages increase the importance of nanotechnology and nanosensors. The use of nanosensors technology to help, guide, and strengthen diagnostic techniques instead of traditional methods in investigating plant diseases can move towards sustainable and precise agriculture and increase the productivity of agricultural and garden crops. The components and type of action of a non-sensor are depicted in Figure 2 [40].

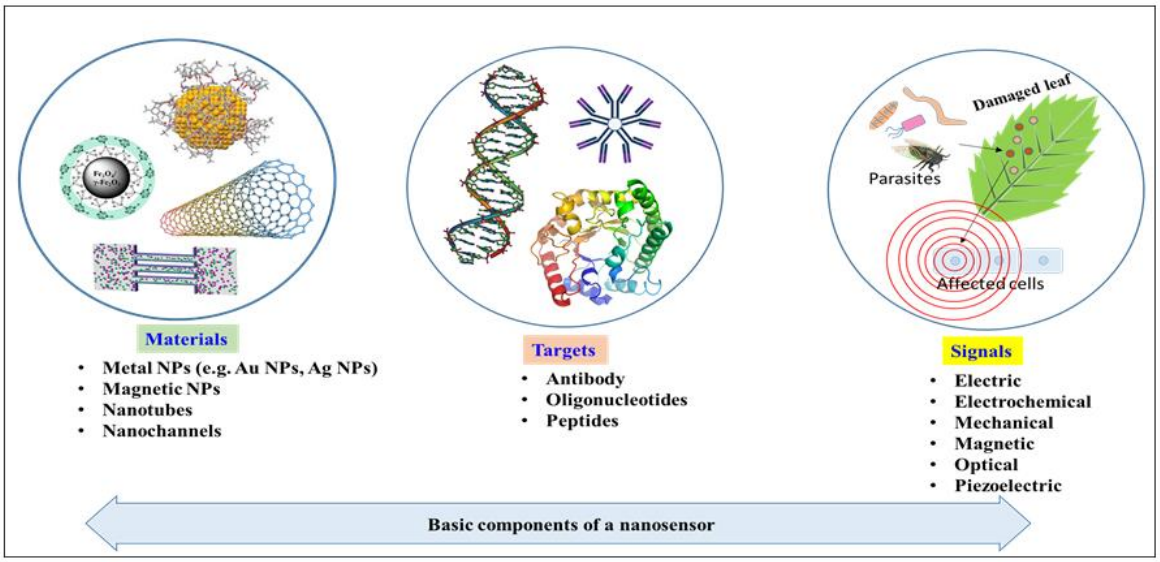

Figure 2. Basic components of a nanosensor. Nanosensors are made of various compounds and can be used to affect molecules such as antibodies, oligonucleotides, peptides, etc. Depending on the type, nanosensors can be used to detect certain signals

Nano-fertilizers

One of the most important fields in the agricultural sector is the field of fertilizers and soil enhancers. Animal manures have been used since ancient times in the agricultural sector to increase crop production. Synthetic or chemical fertilizers including phosphorus and nitrogen fertilizers and other similar fertilizers may cause soil salinity due to their long persistence in the soil, or due to leaching, they cause eutrophication in surface water and increase mineral salts in underground water. Concerning the animal manures, the transfer of weed seeds and plant diseases is also important. Nano-fertilizers can be a suitable solution for the problems caused by fertilizers in agriculture due to their gradual, controlled, and required release, easy dissolution and absorption, or site-specificity (Table 1) [48,49]. In the current era, nano-fertilizers, especially biological nano-fertilizers, have gained a lot of acceptance compared to chemical fertilizers, because these fertilizers are environmentally friendly and cost-effective, and they can be more effective against the increase in food demand with the global population boom. In general, nanotechnology can be used in the design of micro and macronutrient fertilizers needed for plant growth [50,51].

Nano-fertilizers can be defined as nutrient fertilizers with a structure and particle size in the nano range that allows targeted delivery to plants and enables controlled release and effective absorption of nutrients [52]. Unique features such as high surface-to-volume ratio, high mobility, and solubility, target specificity and low toxicity in optimal concentrations that improve crop performance are present in nano-fertilizers compared to conventional fertilizers. By expanding the leaf surface, increasing the speed of photosynthesis and improving the light absorption potential (harvesting of PAR), nano fertilizers can increase the amount of dry matter and thus increase crop production (Table 1). According to their performance, nano-fertilizers can be divided into macro-nutrient nano-fertilizers (hydroxyapatite, nano-urea, nano-calcium, nano-sulfur), micro-nutrient nano-fertilizers (nano-zinc, nano-copper, nano-boron, nano-manganese particles and etc.), and classified nano-fertilizers containing nutrients (such as Chitosan-NPK nano-fertilizers) [51]. In recent years, nanofertilizers have had a tremendous impact on precision agriculture. In precision agriculture, controlled systems are designed that improve the efficiency of using agricultural inputs in terms of time and space. The gradual and controlled release of nutrients in response to the biological needs of the plant is one of the most important advantages of nano-fertilizers, which can greatly reduce the environmental risks caused by chemical fertilizers. Nutrients in nano-fertilizers can be delivered by different methods such as encapsulating nutrients by nanomaterials, covered in a polymer layer, in the form of nano-emulsion or directly as nutrient nanoparticles. The gradual release of nutrients in nano-fertilizers can help reduce soil and water pollution, prevent eutrophication, and protect plants against various abiotic and biotic stresses [53]. In recent years, the production of nitrogen nanofertilizers has been investigated in many researches. Nitrogen gas makes up 78% of the Earth's atmosphere [54]. This element constitutes a vital component of numerous key structural, genetic, and metabolic compounds within plant cells. Nitrogen is an integral part of amino acids, nucleic acids, chlorophyll, and various enzymes, playing a crucial role in energy transfer compounds like ATP (Adenosine triphosphate). Nitrogen exists in the form of organic compounds of nitrogen, ammonium ions (NH_4^+), and nitrate ions (NO_3^-) in nature, which are mostly available to plants in the form of nitrate, but most of the nitrogen is unavailable to plants due to various reasons such as leaching [55]. To overcome this problem, nanotechnology can help humans using appropriate tools. In several studies, zeolite has been used to produce nitrogen-containing nanocomposites. Clinoptilolite zeolite (CZ), a porous mineral with high cation exchange capacity and high affinity for NH^{4+}, has been used to reduce NH_3 emissions from agricultural fertilizer and to eliminate NH_3 toxicity to plants. The use of $(NH_4)_2SO_4$ loaded in nano CZ has been reported to minimize nitrogen leaching and increase nitrogen utilization by crops in sandy soils compared to $(NH_4)_2SO_4$ alone. Clinoptilolite has been reported to not only enhance the efficiency of nitrogen fertilizers, but also decrease nitrate leaching by inhibiting the conversion of ammonium to nitrate through nitrification.

In a specific study, zeolite demonstrated the potential to diminish ammonia volatilization by capturing Ammonium-N at exchange points. The introduction of 6.25% more zeolite resulted in a notable 50% reduction in ammonia volatilization.

Table 1. Some advantages of nanofertilizers over the use of conventional fertilizers

Properties	Nano-fertilizers	Conventional fertilizers
Solubility	High solubility	Low solubility
Adsorption capacity	Lesser	Higher
Bioavailability	High	Less
Nutrient uptake efficiency	High nutrient uptake	Low nutrient uptake
Release of nutrients	Slow and controlled release	Rapid release

In contrast, ammonium bound to zeolite serves as a valuable source of slow-release nitrogen for plants, contributing significantly to increased plant growth while concurrently minimizing nutrient loss to groundwater and the environment, unlike traditional chemical fertilizers [56]. Phosphorus (P) is another element found in nature that plays an important role in the production of agricultural products and nutritional health. Phosphorus plays a vital role in the energy cycle, respiration, and the ATP structure, the structure of phospholipids and proteins, the structure of the plasma membrane of cells, and some enzymes. But as mentioned, the use of phosphorus fertilizers or phosphorus salts aggravates the problem of eutrophication in water bodies. Therefore, the use of nano-fertilizers to control the release of phosphorus materials can be considered as an effective method to achieve precise and sustainable agriculture. Studies have shown that the application of nano-fertilizers compared to soybeans treated with conventional phosphorus fertilizer ($Ca(H_2PO_4)_2$) significantly increases the growth rate and grain yield [57]. In other experiments, fertilization efficiency Phosphorus-based nanomaterials (nano-hydroxyapatite and nano-phosphorus) have been evaluated on tomato (Solanum lycopersicum) compared with phosphate rock, and the results showed that phosphorus-based nanomaterials increase the phosphorus level in all types of soil for tomato plant growth. In addition, by reducing the use of phosphate rock resources, this valuable element can be preserved for future generations of mankind [58].

Another important element and essential micronutrient for plants is zinc (Zn), which is mainly absorbed in the form of a divalent cation (Zn^{2+}). Zinc acts as a cofactor, a metal component and a regulatory agent in many enzymes and is very vital for plant physiological reactions. This element is mainly used as zinc oxide (ZnO) or zinc sulfate ($ZnSO_4 \bullet H_2O/ZnSO_4 \bullet 7H_2O$) to correct zinc deficiency in soil. The use of zinc nanoparticles to overcome zinc deficiency has been considered due to the better reactivity of zinc nanoparticles compared to the bulk form of zinc. In addition, ZnO NPS has been shown to have better antimicrobial activity against various pathogens. In addition, it has been shown in a study that ZnO NPS has better antimicrobial activity against various pathogens [59]. The results of another study showed that when peanuts are treated with ZnO NPs (25 nm), it leads to an increase in seed germination and seedling growth, early flowering and an increase in leaf chlorophyll content, and the pod yield per plant is 34% higher than the plants were chelated with bulk $ZnSO_4$ [60]. In various experiments, the effectiveness of silver nanoparticles (Ag NPs) on wheat, corn, and beans at different concentrations stimulated plant physiological characteristics (stem and root length, leaf area, chlorophyll content, carbohydrates, and protein) [61]. The use of TiO_2 nanoparticles in spinach and soybeans, Si NPs in corn plants, and iron magnetite nanoparticles in wheat as fertilizers has also been proven [62].

Titanium nanoparticles (TiO_2 NPs) have been applied to modify soil salinity in beans. Studies have shown that the low concentration of TiO_2 nanoparticles affects the morphological characteristics of plants and increases the dry weight of the plant. For example, the treatment of different concentrations of nanoscale TiO_2 NPs on rapeseed and wheat seeds increases the seed germination power [63,64]. Other micronutrient nanofertilizers include copper (Cu) nanofertilizers. This element is an essential component in many enzymes and proteins. Foliar application of Cu NPs in different concentrations has been shown to increase the bioactive content of fruits such as fruit firmness, abscisic acid content, and antioxidant content [65]. The next element is iron, which is an essential element for plant growth and plays a vital role in chlorophyll. Most of the iron in conventional iron fertilizers is removed from the reach of plant roots and enters the soil. Iron oxide nanoparticles (Fe_2O_3 NPs) as a nano-fertilizer can be a suitable alternative to these chemical fertilizers. Reports show that when peanut (Arachis hypogaea) is treated with Fe_2O_3 nanoparticles as nanofertilizer, root, stem length, biomass, plant height of peanut plants, and phytohormone content of antioxidant enzymes increase [66]. Due to their nanoscale and magnetic properties, iron nanoparticles in the form of nanofertilizers and nanocomposites are widely used in agriculture and industry to improve contaminated soil and groundwater. Finally, it can be mentioned that most of the elements and nutrients needed by plants can be obtained in the form of nanofertilizers with today's technologies. As mentioned, macronutrient elements can also be used as nano-fertilizers. Examination of wheat plants cultivated in sandy soil with nano-chitosan-NPK fertilizer showed that these nanoparticles cause a significant increase in plant growth and productivity [67].

Nano-pesticides

Pesticides are another group of agrochemicals that are very important in agriculture to fight pests and diseases. Despite the tremendous changes in agriculture and the increase in agricultural production in recent decades, these compounds have challenged mankind due to causing a lot of environmental damage and the spread of various types of cancer [68]. The excessive and unnecessary use of pesticides today has caused the pollution of underground and surface water, damage to wildlife and vegetation, and therefore mankind is looking for a way to limit the use of these types of compounds as much as possible [69]. Therefore, nanotechnology can also help humans in this field. Nano-encapsulation of pesticides causes the active substance of the pesticide to be released gradually, slowly, and in the required amount, thus preventing the loss of the pesticide or its excessive entry into the surrounding environment of the plant [70]. Nanoformulations can be further used as site-specific and applied only to the target tissue. Moreover, nanoemulsion with water or oil increases the solubility and efficiency of pesticides against various pests. So far, various types of nanopesticides have been synthesized. For example, silver nanoparticles (Ag) as an active agent with a wide spectrum against various plant pathogens such as *Biploaris sorokinniana*, *Botrytis cinerea*, *Colletotrichum gloeosporioides*, *Fusarium culmorum*, *Phythium ultimum*, *Phoma, Megnaporthe grisea*, *Trichoderma sp.*, *Scalerotinia sclerotiorum*, *Sphaerotheca pannasa*, and *Rhizoctonia solani* has been used. In addition, the very good effect of silica nanoparticles with silver (SiAg NPs) against powdery mildew disease in cucurbits has been reported. Nano-porous silica has also been reported as a validamycin carrier [71]. In some studies, the effect of copper nanoparticles (Cu NPs) with low concentrations on Gram-positive and Gram-negative bacteria and fungal pathogens such as *Fusarium sp., Phytopthora infestance, Xanthomonas oryzae*, and *Xanthomonas campestris* has been reported [72,73]. Zinc nanoparticles (Zn NPs) are mostly reported as nanofertilizers, but in some cases, antifungal activity of these nanoparticles has been recorded against *Penicillium expansum*, *B. cinerea*, *Aspergillus flavus*, and *A. niger* [74,75]. Similarly, in other studies, the strong effect of nano sulfur and nano hexaconazole formulation against plant pathogenic fungi such as *R. solani*, *Erysiphe cichoracearum*, and red spider mite *Tetranychus utricae* has been reported [71].

Other important agrochemicals include herbicides. Herbicides have caused a lot of damage to all types of vegetation in this world due to their heavy use in recent years. Currently, nanoherbicides are being developed to address a variety of weed problems because nanotechnology can be used to improve the performance of many existing herbicides or to formulate an alternative that is fast, efficient, and economical [76,77]. Nanoherbicides as a "smart delivery system" offer an environmentally friendly approach. These substances reduce the damage to the environment by reducing the introduction of herbicides into nature and controlling the time or area of the release of the active ingredient of the herbicide [78]. In the new era, chitosan can be used as a supplement for the production of pesticides (herbicides, fungicides, bactericides, insecticides, and acaricides). Chitosan is a non-toxic, biocompatible, biodegradable polymer, and is abundantly found in nature, crustacean shells, and some fungi [79,80]. Chitosan can also induce resistance in plants [81,82]. Utilizing copper-chitosan nanoparticles serves as a stabilizer and masking agent, enabling the production of herbicide with controlled release. In addition, formulations incorporating chitosan, starch, and alginate were employed to reinforce and develop slow-release compositions for the imazaquin herbicide [83]. A composite gel, consisting of carboxymethyl chitosan (CM-chit) and bentonite (H-bent), serves as a carrier for encapsulating atrazine and imidacloprid. This system is designed to regulate their release in water and postpone their leaching into the soil [5,84].

According to this study, the composite carrier has the potential to decrease the leaching of pesticides, offering a valuable approach to mitigating the adverse environmental impacts of pesticides. Research findings demonstrate that formulating paraquat with alginate/chitosan nanoparticles alters the herbicide's release characteristics and its interaction with soil. This suggests that this system could serve as an effective method to minimize the adverse effects of herbicides on the environment [85]. In a separate investigation, composite hydrogel beads comprised of chitosan (Cht), alginate (Alg), and cenosphere (Cn) were examined for the sustained release of imidacloprid (IMI), providing additional benefits such as UV protection for the pesticide, suitability for direct field application, and potential upgradability. The findings revealed that the IMI@Cht-Alg-Cn beads exhibited a substantial encapsulation efficiency of approximately 80%, attributed to their hollow structure and porous network [86].

Conclusion

The need to increase agricultural production is becoming more pressing as the human population grows. However, this increase in production must occur on existing agricultural land. Agrochemicals, such as chemical fertilizers and pesticides, have revolutionized agriculture and increased production in recent decades. However, these agrochemicals have caused significant damage to the environment and living things on earth. To reduce the environmental effects associated with the use of these substances, nanotechnology, such as controlled release nano-formulations, can be a possible alternative to conventional methods. This approach ensures that the required active substance is used in the required amount, at the right time, and in the target area. Various nano-based technologies can also be used in water treatment systems, gene transfer to plants and animals, the production of nano-sensors to detect pests and diseases, and finally, in moving towards sustainable and precise agriculture. Pesticides are extensively employed in the developing world, with an increasing demand driven by the prevailing crop production system. Herbicides, insecticides, and fungicides play a crucial role in safeguarding crops against weeds, insects, and diseases. Nevertheless, the application of these substances is met with societal apprehensions. Despite well-documented health and environmental risks, the global consumption of pesticides continues to rise. Pesticides are indispensable in agricultural production, but they have caused significant damage to the environment. With all the mentioned cases, it can be mentioned that nanotechnology can revive human hopes for environmental restoration and reduce the risks of hazardous materials in nature by modifying chemical compounds.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

Credit authorship contribution statement

Conceptualization, J.F.G and E.S: methodology, J.F.G: writing -original draft preparation, E.S: writing -review and editing, and P.B: design Figures and editing. All authors have read and agreed to the published version of the manuscript.

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