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Nanotools of ZnO Nanostructures offered by Nanotechnology for Sustainable Farming

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***Abstract:** The field of nanotechnology has been growing immensely having its application in health, automobile, defence and agriculture sectors. Recently in a decade its role has been explored and analysed in agriculture sector to comply the demanding needs of food with increasing population. This can be achieved by enhancing crop yield, maintaining air, water and soil quality, managing the resources and harvested food. Nanosensors can help in attaining them with high efficacy and specificity. They allow precise monitoring of plant growth with efficient use of resources, and provide timely detection of plant diseases, air and soil contamination by keeping check on pathogens. By using internet and computer technology the data can be collected and assessed to take corrective and curative measures instantly, allowing good management. Here we discuss ZnO based nanostructures, their cost effective methods of synthesis, role as nutrient source, nanosensors to keep check on pathogens, contaminants in air, water, pesticide and moisture of soil. By proper care and monitoring of crops on real time basis and keeping agro-ecosystem safe with cost effective nanotools, we shall achieve a boost in crop productivity.*

***Keywords:** Agriculture, Bioreceptors, Environment, Fertilizers, Hydrothermal, Heavy metals, Micronutrient, Nanomaterials, Nanosensors, Nanostructures, Nanotools, Pesticides*

I. INTRODUCTION

Agriculture sector is vital source of sustenance for human population providing food security, economic opportunities, and environmental benefits. Agriculture's direct contribution to global GDP is approximately 4%. In least developed countries, it can have an even more substantial impact on the economy, often accounting for more than 25% of the GDP. Hence, important for survival and growth of mankind. The agricultural production system has to be constantly monitored and improved in order to sustain the rising population of the globe. By 2040, about 9.1 billion people will need to be provided with food . Also due to pollution and erosion one third of arable land has been lost in last 4 decades. Thus, in order to use the limited land available for the growing population and to avoid scarcity of food resources, sustainable farming is required [1]. Fig 1 shows objectives of sustainable agriculture. Constant monitoring of the crop, air, soil, residual pesticide and moisture in soil will help agriculture to be managed effectively and efficiently saving our resources. This can be achieved by nanosensors for maintaining soil nutrients, adequate moisture in soil, pH of soil, temperature in green house plantations, and morphology of plant[2]. It will aid in taking quick and correct decisions for proper care. Nanosensors are nanotools, an application of nanotechnology that can be used by farmers to improve fertilization for higher yield.

Fig. 1 Objectives of sustainable agriculture

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A. Nanotechnology

Nanotechnology can be a promising tool to achieve food safety, boosting crop yield and providing sustainability. Fig. 2 shows schematic diagram of role of nanotechnology in agriculture. Nanotechnology aids in superior agricultural production by providing nutrients and pesticides in form of nanoparticles [3]. This can be achieved by using the nanostructures of metal oxides or grapheme oxide which encapsulate the nutrients to be distributed. These nano nutrients or nano fertilizers can be synthesized and released in soil according to the need of the plant. A steady and slow release of nutrients is accomplished when the fertilizer particles are coated with nano membranes. Recently plant-microbe-engineered nanoparticles PM-ENPs is new venture of nanotechnology where plant or microbe cell is used to synthesize or tailor the metal NPs [4] . PM-ENPs have good anti-microbial activity, help in enhancing the plant growth by utilising nutrients in regulated amounts. Nanosensors is one of the application of nanotechnology having at least one of the sensing dimensions of the nanosensors less than 100 nm. These sensors allow interaction of sensor to the target at a nano scale. It results in high sensitivity and the target can be detected in 1 count parts per million. They have high surface area-volume ratio that's why these sensors are not only cost effective and handy but also highly specific, highly sensitive, small size, and detect target at considerably lower level [5]. To improve the sensitivity, the nanosensors are binded with biological molecules called bioreceptors like aptamers, proteins, enzymes, nucleic acids, cells. These bioreceptors are utilized to recognise the target and result in production of output measurable signal. The probe, transducer and detector are major components of a biosensor. The probe consists of bioreceptors. Transducer is the nanostructures of metallic oxides, graphene, polymers which convert the biorecptor –analyte interaction signal into measurable signal. Nanosensors can be used in plant pathogens diagnosis [6]. The nanosensors can be implanted on the plant to check the structural change in the plant and environment around itself. Bhawna et al has reported on electrochemical sensors for agriculture application [7].

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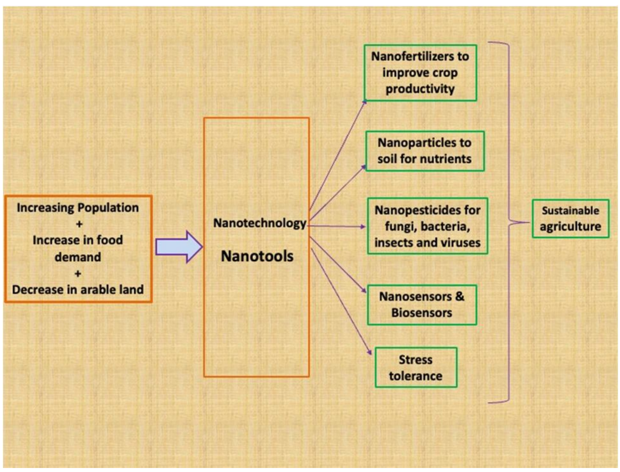

Fig.2 Role of nanotechnology in achieving sustainability in agriculture

B. Nanomaterial - ZnO

Various nanosensors based on nanomaterials like lead zirconate titanate, graphene CNT, polymers and metal carbides, nitrides and oxides have been introduced in the industry . The major challenges is to look out for a nanomaterials that offers characteristics of high stability, sensitivity, nontoxicity, biocompatibility and cost-effectiveness. Due to the growing environmental concerns and demand for developing multifunctional devices in cost effective way there has been a push to develop semiconductor materials like ZnO. ZnO possesses, extraordinary electronic & chemical properties like wide bandgap (3.3 eV), and large exciton-binding energy (60 meV) at room temperature. It also exhibits high thermal conductivity and electron mobility. It absorb ultraviolet (UV) light in the wavelength range of 200 to 350 nm. The emission wavelengths of ZnO typically range from the near UV region (around 380 nm) to the visible spectrum (up to approximately 700 nm). As a result it holds promising catalytic, electronic, optical and piezoelectric properties [8]. Moreover due to its low toxicity and biodegradability, it is environment friendly material of interest at present. ZnO nanomaterials are easy to fabricate as easy availability of raw materials and precursors .

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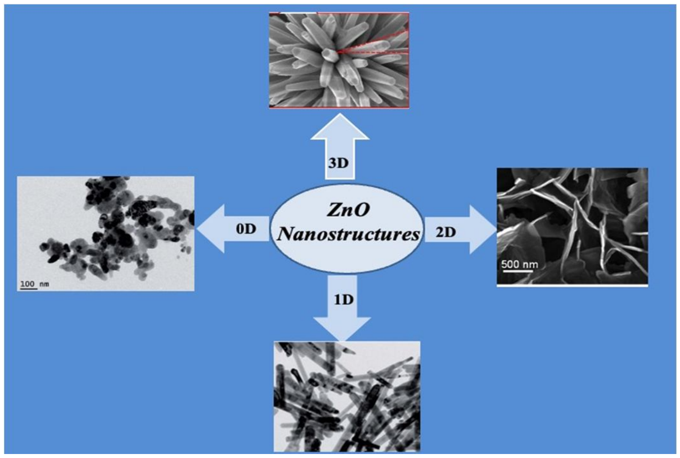

Fig.3 Images of ZnO nanostructures categorised on basis of their dimensions

Fig 3 shows images of ZnO nanostructures categorised on basis of their dimensions and Table 1 shows characteristics and applications of ZnO nanostructures. ZnO nanostructure fabrication allows easy integration with Silicon nanodevices to obtain cost-effective multifunctional sensors [9]. In this paper we review on current status of ZnO nanostructures as nutrient source and as nanosensors for detection of plant pathogen and pesticide and for monitoring soil conditions.

Nanomaterial	0D, Zero-dimensional ZnO	1D, One-dimensional ZnO	2D, Two-dimensional ZnO	3D, Three-dimensional ZnO
Size	All dimensions<=100nm	Two dimensions<=100nm	One dimensions<=100nm	All dimensions>100nm
Characteristics	ZnO NPs exhibit zero-dimensional confinement of electrons. Electronic properties are restricted in all three dimensions. As the nanoparticle size decreases, the bandgap of ZnO rises, resulting in changes in its optical and electronic properties	These nanostructures are characterized by their elongated shape, with length dimensions much greater than their width and height dimensions. ZnO exhibits enhanced properties due to quantum confinement effects, high surface-to-volume ratio, and reduced dimensionality.	Nanostructures possess a thickness in the nanometer scale while having larger lateral dimensions. They have quantum confinement effects, large surface-to-volume ratio, and tunable bandgap of ZnO nanostructures.	These nanostructures exhibit unique properties such as efficient light (scattering due to defects and porous structure), improved charge carrier transport and enhanced surface area.
Application	Optoelectronics, photocatalysis, sensors, and energy storage.	Field-effect transistors, chemical sensors	Nanosensors.	Nano sensors, Li ion batteries, biosensors
Example	Nanoparticles[10] Quantum dots	Nanowire (NW), Nanorod (NR) [11]	Nanofilm, Nanosheet(NS) [12]]	Nanotetrapod, Nanoflowers[13]

Table 1 ZnO nanostructures are divided on basis of dimension showing characteristics, applications & examples

II. SYNTHESIS OF ZNO NANOSTRUTURE

Nanostructured ZnO surfaces can be physically and chemically tailored to attain high performance through various synthesis route. ZnO nanostructures morphology, crystal structure, size, surface polarity, can also be tuned as they affect electron transport in the system. New generation synthesis route for ZnO nanoparticle have been reported known as green synthesis via sol-gel using bio extracts (aqueous fruit extracts) for biological and environmental applications [14]. The cost effective and most common methods of synthesis are discussed here. Synthesis of ZnO nanostructures mainly consists of chemical and physical methods. Few famous techniques are the sol–gel method, hydrothermal thermal method, chemical vapour deposition and physical vapour deposition.

A. Sol Gel

This technique is used to synthesize nanoparticles by wet chemical route by nucleation phase and growth phase. In this method, the molecular precursor like metal alkoxide (Zinc acetate) is dissolved in alcohol (ethanol) to form a sol. By hydrolysis process the sol is converted to gel by heating and continuously stirring process. Sols, prepared from precursors and solvents are colloidal solution. They consist of solid particles of nanometer size suspended in the liquid phase. Gels are formed by condensation process followed by aging for phase transformations to solid. The gels are dehydrated at temperatures around 600 ^{o}C to form xerogels and nanoparticles. Zero-dimensional ZnO nanoparticles of high purity and uniform size can be produced. Precursor concentration, aging of sol, pH of the solution and the thermal treatment affect the morphology of nanostructures[15]. Its advantages are uniformity of thickness. simplicity, cost-effective process and large area coating. The disadvantage is long processing time and complex reactions are involved.

B. Hydrothermal

Hydrothermal is aqueous chemical growth where vertically oriented nanowires grow on a substrate. Precursor solution is prepared by dissolving zinc salt, such as zinc nitrate [$Zn(NO_3)_2$], zinc acetate [$Zn(CH_3COO)_2$] in deionized water. Basic solution like ammonium hydroxide is added to adjust the pH. Precursor solution is transferred into a reaction vessel, such as a Teflon-lined autoclave. The reaction vessel should be able to withstand high temperatures and pressures. The reaction time in hydrothermal reactor can vary from a few hours to several days. ZnO crystal has hexagonal lattice structure. When nanoparticles come into contact, they align themselves along specific crystallographic directions due to the preferred bonding arrangement of atoms within the ZnO lattice. As the nanoparticles merge, they form elongated structures with a rod-like shape, resulting in nanorods[4]. The nanostructures are washed with a suitable solvent, such as ethanol or deionized water. Hydrothermal technique is safe, and environmentally friendly. Advantages are high crystallinity, high purity nanostructures and easy operation. Disadvantages are expensive equipment and high temperature and long processing time.

C. Chemical Vapour Deposition

CVD involves chemical reaction in vapour phase. Here Zn vapor is generated by heating the Zn powder at high temperature. It binds with Oxygen to produces ZnO NPs on the substrate. The CVD method involves the deposition of thin films or nanostructures by the reaction of precursor gases on a substrate under controlled temperature and pressure conditions. Precursor used are metalorganic compounds (e.g., zinc acetate, zinc acetylacetonate) or inorganic compounds (e.g., zinc nitrate, zinc chloride). The CVD has a reaction chamber with a substrate holder, precursor gas sources, a heating element, and a pressure control system. The substrate is heated in the range of 300-800°C. A carrier gas, such as nitrogen or argon, is introduced into the reaction chamber to create a controlled atmosphere and carry the precursor vapors to the substrate. The precursor vapors decompose on the heated substrate, releasing Zn and O species. These species recombine and form ZnO nanostructures on the substrate surface. Parameters like temperature, pressure, gas flow rate affect the crystallinity of film. High-quality, crystalline nanomaterials are produced by this method [16]. Disadvantage : high temperature processing and organic exhaust can be toxic to environment.

D. Physical Vapour Deposition

In PVD technique thin films or coatings in large scale can be deposited through the condensation of vaporized material. It offers excellent control over the growth of nanoparticles, allowing for precise tuning of their size, shape, composition, and structure. Solid source material is placed in a vacuum chamber, where it undergoes vaporization. The vaporization can be achieved through various methods such as pulsed laser deposition, sputtering, electron beam and thermal evaporation, depending on the specific requirements of the nanoparticle synthesis. Molecules of vapourised material then travel through the chamber and interact with the substrate, kept at a lower temperature and gets deposited on it.

By controlling the deposition parameters such as temperature, pressure, and deposition time, the nanoparticle morphology and size can be effectively controlled. Disadvantage: process uses complex equipment, with a very high cost and deposition rate is quite slow [18].

III. APPLICATIONS

A. ZnO Nanoparticles for Nutrients and Fertilizing [19]

Zn is important micronutrient required by plant for cellular and physiological activities of plants. Plant needs several other nutrients for growth and well-being, which it absorbs from soil and water through roots . Over the years with continuous use of land for cultivation, and various other reasons like pollution, the soil gets depleted of nutrients. Replenishment of soil is done by chemical fertilizers. But over dose of these fertilizers may reduce soil fertility. The traditional fertilizers release the excess N and this spawns climate change as it contaminates the environment. New innovation in nanotechnology is nano fertilizer. This nanotool offers large surface area of interaction with the plant cell , thereby increasing reactivity and higher probability of absorption by the plant root. Moreover it is more environmental friendly and provide good ecologically treatment for plant and soil by providing Zn ions as micronutrients. By coating the fertilizer particles with ZnO NPs, the nutrients can be released gradually over time, providing a sustained supply of nutrients to the plant. This can result in reduced fertilizer application rates, lower the cost. It prevents wastage of fertilisers due to leaching or evaporation by quick absorption. The nanocapsules and nanoparticles of ZnO provide a systematic way to dissemante fertilizers in regulated amounts [20] and are highly target specific. Thereby providing high specificity and perseverance of the resources. [21]**.** The nanofertilizer enhance the process of seed germination, root growth, photosynthesis rate. They increase chlorophyll content in leaves and thus boost grain yield. It has been reported that ZnO nanofertilizers also enhance plant forbearance to abiotic stresses such as heavy metal toxicity, salinity and drought. [22]. It was found that when peanut seeds are processed with varying concentrations of zinc oxide nanoparticles it boosted seed germination increased root and stem growth and enhanced the over all growth of the plant. Lijuan Zhao et al. used ZnO NPs to enhance the nutrition of cucumber [23]. He used Zn-fertilizer NPs suspended in a biopolymer film, ready for stable dispersal and distribution. Adhikari et al reported that pigeon pea seeds, soyabean, maize coated with ZnO NPs resulted in better seed germination and plant growth [24]. K. Włodarczyk et al also reported the result of nano-ZnO on seed germination in tomatoes[25].

B. ZnO NPs for Nanopesticides

Crop pests are microbes like bacteria, fungi, viruses etc. damage crop by hampering their growth and inducing diseases. This decreases the crop production and results in wastage of resources. As a result annually there has been loss of crops worth $220 Billion [26, 27] . In order to battle the pests and control them, heavy use of chemical pesticides are used which have adversely affect the environment as well as the human beings. Moreover the pests develops resistance against them. The nano pesticides based on ZnO are used as fungicides, bactericide , insectides etc. The nanoparticles penetrate the pests' cuticle or cell membranes, damage the cell, disrupts physiological processes, and kills it. They have least adverse impact on the ecosystem. They are environmentally friendly, used in small amount and are highly specific. The large surface to volume ratio of nanoparticles allow increased contact with pests, leading to improved pesticidal activity with high efficacy. For proper disperse and adhesion to pests, the ZnO NPs, are encapsulated by biodegradable polymers. Wani et al published antifungal activity of ZnO and MgO. It inhibited germination of spores of fungi, Rhizopus stolonifera [28]. B. Malaikozhunda et al reported that Pp-ZnO NPs impeded the growth of pulse beetle, in stored grains [29]. Lili He et al reported that ZnO NPs hampered development of pathogenic fungi Penicillium expansum [30].

C. Monitoring of Soil Nutrients

ZnO nanosensors help in monitoring soil nutrients due to their unique properties and sensitivity. They can detect and measure various soil nutrients, including nitrogen, phosphorus, potassium, and micronutrients such as zinc itself. ZnO biosensors can be used to measure soil nutrients such as potassium, phosphorus and nitrogen. The ZnO nanosensors can be functionalized with specific receptors or ligands that selectively bind to the target soil nutrient. The ZnO nanosensors are then applied to the soil either by direct mixing or by embedding them in a matrix, such as hydrogels, which can be easily dispersed in the soil. Sensing mechanism is based on interaction of ZnO nanosensors with the target. Chemical reactions takes place and this results an electrical signal and thus data is acquired and analysed Real-time information on soil nutrient levels can be received by farmers in order to optimize fertilizer application. This will reduce waste, and improve crop yields. Akshya et al reported real time sensing of potassium in soil using ZnO-multiwall carbon nanotube-based sensors [31].

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D. Detection of Crop Diseases

ZnO biosensors can be used to detect plant pathogens and diseases early, allowing farmers to take corrective measures before the diseases spread and cause significant damage. This can help reduce the use of harmful chemicals and pesticides, which can be detrimental to both the human health and environment. ZnO-based biosensors can detect crop diseases by utilizing the specific interactions between the target pathogen or disease biomarkers and the surface of the ZnO nanomaterial. These interactions can result in changes in the electrochemical, optical and electrical properties of the ZnO, which can be measured and analyzed. To boost the sensitivity and selectivity of ZnO-based biosensors, the surface of ZnO is often functionalized with specific bioreceptors or recognition elements like antibodies, enzymes, DNA. Based on the transduction principle of ZnO the disease/pathogens can be detected by electrical technique-FETs or impedance spectroscopy techniques, optical technique - fluorescence spectroscopy, electrochemical techniques - amperometry, voltammetry and gravimetric technique. Cardoso et al [32] has reviewed the plant pathogen detection by various nanomaterials. Formaldehyde (FA) is produced by microbes and plant decomposition. Quartz crystal microbalance QCM sensor based on gravimetric technique detects FA with detection limit of 41 ppb, using nanofibers of CuO/ZnO composite. Porous structure and big surface area of nanofibres helped in greater access of the analyte formaldehyde.

E. Detection of Heavy Metals and Residual Pesticides

Due to excessive use of conventional pesticides around 26 million humans per annual are casualties of pesticide poisoning globally. This results in about 220K mortality annually. The growing concern of excess pesticides use brings to find alternate solutions. To keep check on their quantity , nanotools like ZnO biosensors can be used to detect residual pesticide, heavy metals in the soil, water, and crops. This is important because heavy metals can be toxic to plants and can accumulate in the food chain, posing health risks to animals and humans. Hydrothermally generated porous nanostructures (nanotubes, nanoplates) of ZnO based nanosensors were fabricated to detect the heavy metals (Pb, Cd, Hg) [33]. Dibakar Sahoo fabricated nanosensor for nanosensing of pesticides at concentration of ~4 ppm in water by Zinc Oxide Quantum Dot [34].

F. Nanosensors for Pathogens Detection

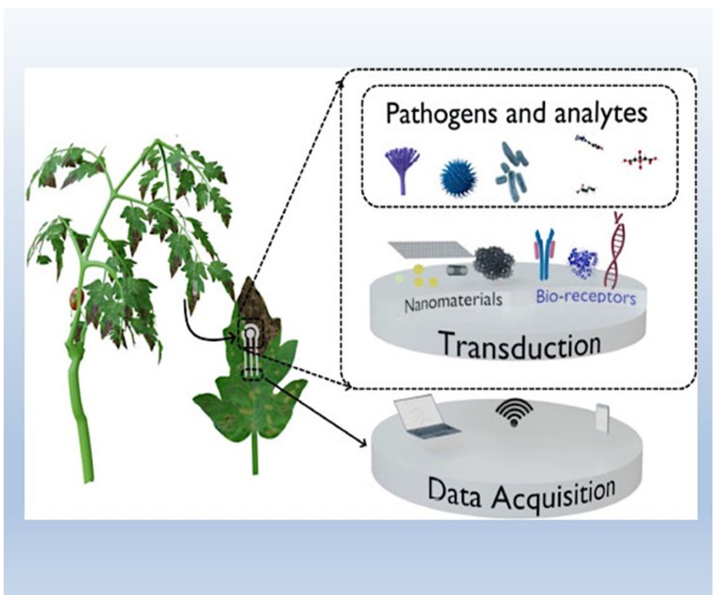

Fig 4 Illustration of nanosensor implanted on leaf to detect targets like pathogens [35]

Nanosensors for plant pathogen diagnosis are microneedle patches, nano diagnostic kit equipment, quantum dots, nano biosensors/barcoding and array based nano sensors. They help in constant supervision of crop, field, pest and abiotic stressors. Fig. 4 shows schematic illustration of nanosensor on plant to detect pathogens. Alla et al reported optical biosensor developed, for pathogen grapevine virus A-type (GVA). Here ZnO thin film was immobilized with antibodies [36] to detect the virus. Siddiquee et al. evolved a nanobiosensor to detect fungi Trichoderma harzianum using ZnO NPs/chitosan[37].

G. Monitoring of Environmental Factors

ZnO based nanosensors can be used to monitor environmental factors such as gas, temperature, humidity, and light intensity[38]. This information can help farmers to take decisions about irrigation, harvesting.

Nanosensors for environment pollutant gases like H_2S, NH3, NO_2. Prolonged exposure to NO_2 can result in insufficient chlorophyll synthesis which can result in chlorosis. And more exposure can decrease the rate of photosynthesis. Rajesh et al reviewed on ZnO nanostructures for NO_2 gas sensing [39].

Water scarcity is major problem. Agriculture water consumption accounts for 70% global water usage. In order to avoid wastage of water and use it efficiently, sensors can be used to provide information about status of soil moisture content precisely. The sensing mechanism of ZnO nanosensors is built on the change in electrical conductivity that occurs when the nanosensor is exposed to moisture. The ZnO nanosensors can be integrated with wireless sensor networks for real-time monitoring of soil moisture. The wireless sensor networks provide accurate information to farmers on the soil moisture content. This information can be used to optimize irrigation practices, reduce water usage, and increase crop yields.

IV. CONCLUSIONS

ZnO based nanomaterials like nanoparticles, nanofibres, nanorods are used as nano - nutrient sources and nanosensors. They are nanotools offered by nanotechnology that can be adopted in current farming practices. ZnO NPs are used as source of zinc for plants by applying them directly to the roots in soil or through foliar spray. It allows improved Zn uptake due to increased reactivity and solubility. They are target specific and prevent wastage and are thus cost effective. They have quick absorption by plants, reduce fertilizer usage, and thus increase crop yields. ZnO based nanosensors can be placed in the field to determine the crop pathogens and monitor the status of environment. They provide disease protection by being antifungal and antibacterial. The real-time sensors monitor temperature, harmful gases, soil moisture, air contaminants physically. They are able to detect residual pesticides, quantify toxins and fertilizers in water. They facilitate reliable, quick and prior prediction of crop diseases. Thus at present with changing environmental conditions and our ever growing needs, agriculture sector needs extra attention and study. Application of nano technology with new nanomaterials, nanotools assures efficient use of resources, cost saving, prior detection of diseases, high crop yield.

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