Chapter 9

Nanotechnology in Agricultural Practices: Prospects and Potential

N.G. Giri¹, N.S. Abbas² and Saroj Kumar Shukla²*
¹Department of Chemistry, Shivaji College, University of Delhi, Delhi-110027, India
²Bhaskaracharya College of Applied Sciences, University of Delhi, Delhi-110075, India
*sarojshukla2003@yahoo.co.in

Abstract
The novel features of nano confined materials properties are widely explored in several agricultural practices i.e. seed coating, soil conditioning, preservatives and packaging of agro based products. The evolution of materials properties due to nano confinements like controlled degradability, solubility, responsiveness, gas barrier and porosity has added several suitable advantageous features in agriculture practices to help the farmers, traders, consumers and policy makers. In the context of the above development, the present chapter describes the basic features of nano materials to use in agricultural practices along with their impact and effectiveness. Further, the suitable scheme and illustration are used on the basis of available literatures to make the subject lucid and effective along with existing challenges.

Keywords
Nanomaterials, Properties, Soil Nutrient, Protection and Monitoring

Contents
Nanotechnology in Agricultural Practices: Prospects and Potential........252
1. Introduction..................................................................................................................253
2. Nano technology in agriculture ...............................................................254
3. Applications........................................................................................................256
   3.1 Valorization of agricultural wastes and management ................256
   3.2 Soil nutrient and Fertilizers .................................................................259
   3.3 Sensing and monitoring.................................................................261
   3.4 Crop protection and storage..........................................................264
1. Introduction

Recent scientific study reveals that the nanotechnology has efficacy to positively impact on the field of agricultural practices to minimize the adverse problems of agricultural practices on the environment, economy, and human health. Food productivity, soil management, storage and safety [1]. The potential of nano technology and materials promises to irradicate the hunger and maintain the food security for world community along with monitoring soil condition and food quality [2]. Pertaining to this different novel nanomaterials are used in agriculture are polymeric nano composite, nano hydrogel, lipid nanoparticles and inorganic and organic nano materials developed by using different nano fabrication techniques i.e. top down and bottom up [1]. One of the other important use of nanoparticles is in recycling and valorization of agricultural wastes with objective control pollution and their judicious conversion into adsorbent, fertilizer and other organic compound after using different thermo-chemicals, mechano-chemical, physio-chemicals and biochemical treatments [3]. Although, the recycling of crop wastes is a natural process and practiced by farmer since ancient time but the current development in nano technology improves the efficiency of these methods along with better projection of these project into commercial scales [4-5]. The importance of these areas yields exponential increasing trends of publications i.e. research publications, review and patents, which is depicted in Fig. 1.

![Figure 1. Publication frequency trend on nanomaterials in agriculture (www.scopus.com)](image-url)
This exponential increase in publication frequency is confirming the growth of field and need of more and more research studies for commercialization of nano technologies in agriculture practices for economic growth and commercialization. In this context, several reviews and book chapter are published but its update in the form of book chapter is still demand for educating researchers and scientists. In the context of above development, present book chapter describe the updates about the nano technology, nano materials and their applications in agriculture practices. The advantageous features of nanotechnology influenced agricultural practice are discussed with the help of scheme and illustrations.

2. Nano technology in agriculture

In general, the nanotechnology deals the physics, chemistry, fabrication and engineering of materials in the scale of 1 to 100 nm. This materials dimension so important to create a materials transition due to properties confinements’ related Bohr radius, and it generates the unique surface reactivity, sustained degradability, functionality and responsiveness to use in different aspects of agriculture and agricultural practices. The use and practice of nanomaterials and nanotechnology have been created second revolution in agriculture practices and industries with the significant benefit to each stake holders [6-7]. Although, the concept of nano technology has been frequently used by natures as phytochemical biology, biochemistry and properties but its commercialization is a newer development for improved production and processing of agricultural products. The basic need of this technique is with evolving problems in conventional agriculture like limit of conventional farming and nutrient management, and it has invited the scientist to explore the use on nano technology for sustainable advances in agriculture and practices. In this context nano chemist has designed and developed several pristine and hybrid nano materials with tunable chemical and physical properties. Some of the significant nano structured materials used in agriculture practices along with their brief properties and applications are listed in Table 1.

<table>
<thead>
<tr>
<th>SN</th>
<th>Nano materials</th>
<th>Properties</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydrogel</td>
<td>High water retaining capacity with excellent mechanical flexibility</td>
<td>Alternate source of water in soil</td>
</tr>
<tr>
<td>2</td>
<td>Nano coating</td>
<td>Improved mechanical strength with gas barrier.</td>
<td>Seed coating and active packaging</td>
</tr>
<tr>
<td>3</td>
<td>Nano particles</td>
<td>Large surface area and reactivity</td>
<td>Fertilizer and soil nutrients</td>
</tr>
<tr>
<td>4</td>
<td>Nano polymer composite</td>
<td>Tunable biodegradability, reactivity and conductivity</td>
<td>Sustained released and monitoring of soil nutrients.</td>
</tr>
</tbody>
</table>
These nano materials prepared after using different bottom up and top down methods with their own inherited advantages and disadvantages. The comparison of both methods in the term of synthesis used for preparation of nano particles has been illustrated in Fig. 2.

Figure 2. The comparison of preparative methods of nanoparticles

In general, the top down method deals with physical methods like evaporation, sputtering, ablation and ball milling, while the bottom up method includes precipitation, solgel, hydrothermal, LB and reverses micelles. Further, to avoid the agglomeration both hard and soft templates are used with their own inherited merit and demerits. Furthermore, during the preparation of hybrid form of different nano materials, integration of both the techniques are exercised after optimizing the processing condition. In an example, the different templates both hard and soft are used in order to control the aggregation of additives along with influenced dispersion of dispersion phase into dispersion matrix [8]. Thus, a dispersed additive in polymer matrix develops several innovative synergistic features for applications in agriculture for coating, controlled release of nutrient, sensing agro-chemicals and preservatives. Thus, different applications of nano technology and
nano materials in agriculture are shown in Fig. 3. The basic properties makes nanomaterials superior than conventional materials are high surface area, reactivity, responsiveness and retaining capacity for use in different applications like genetic modification, targeted delivery, crop protection and nano fertilizer [9].

Figure 3. Schematic presentation for application of nano materials in agriculture

3. Applications

3.1 Valorization of agricultural wastes and management

Term “valorization” refers the industrial processing, recycling, and reuse of used agricultural products like seed husk, cake, straw and peels. In general the natural uses of agro waste are vermi composting to convert into fertilizer, fodder and microbial degradation into several value added products [10]. However, it current time after realization the corporate social responsibility, it is very important to increase the consciousness towards conversion of huge quantities of agricultural food and agro wastes into different value added product not only to meet the environmental problem but also increase the financial gain of all stake holders. The reduction in food wastage would not only circumvent the burden on availability of natural resources but also help to raise food production for insuring food availability [11-12]. The basic routes and importance of reuse and valorizations of agro wastes are shown in Fig. 4.
In this process the significance nanomaterials are to provide catalysts, facile conversion process, better yields and to control the environmental issue, economy and society [13-14]. For example, the ligno cellulose biomass present in agro wastes are explored for production of biofuels, organic acids, protein enriched feed, bioactive secondary metabolites, aroma compounds after using different nano materials. [15-16] The physio chemical treatments of agro waste also yield several nano materials to use as fertilizers, pesticides, filters, sensors, and photocatalysts with improved properties [17-18]. The potential of agriculture waste valorization has attracted the attention of technocrat to design several biochemical reactors to valorize agro wastes like rice husk into aromatics by thermolysis in the presence nano catalysts like zeolites [19-20]. The proposed experimental set up for effective conversion of rice husk into aromatics is shown in Fig. 5. The diagram is containing three reactors R1 CH4 decomposition reactor; R2 thermal conversion reactor and R3: for upgrading the pyrolysis vapor.

Similarly the presence huge biopolymer like proteins, starch, cellulose and carbohydrate are explored for preparation of bionano composites, biochar, and activated carbon and carbon nanostructure with significant economic valorization [21-23]. Further the nanotechnology induced transformation of organic agro waste cotton fibers and cellulose are good option to convert into biofuel like ethanol due to global increase into price of maize [24-26]. Here, the nano engineering tool increases the performance of the enzymes (α-L-arabinofuranosidase, α-fucosidase, α-galactosidase, β-glucosidase, β-xylosidases, endo-galactanase, β-galactosidase and β-mannosidase during conversion of cellulose into ethanol [27].The technique has been explored by major countries for production of bio-ethanol and a comparative picture is given in Figure 6. Further, nano technology has been also used to prepare different nano particle like cellulose nanocrystals from different agro wastes like corn husk, rice straw and bamboo pulp using nano technology induced acid hydrolysis [28-30]. The significant properties of nanocellulose are transparency, tensile

Figure 4. Illustrative importance and methods for recycling of agro wastes [10]
strength, low coefficient of thermal expansion, which make it suitable to use as reinforcement for polymers, pharmaceuticals, biomedical, fibers and textiles, antimicrobial films, supercapacitors [31]. The conversion processes use some hazardous chemical like chlorinate solvent for bleaching and sulfuric acid in hydrolysis, hence the efforts are made to integrate the principle of green chemistry and green engineering during valorization and recycling [32]. In this regards, Shukla et al has reported the use of hydrogen peroxide a greener solvent to prepare nano sized cellulose to use a reinforcing agent. Thus, obtained cellulose was used to prepare polyvinyl alcohol film to replace non-biodegradable plastic film with heat seaising behaviour [33].

Figure 5. Schematic diagram of the experimental setup to valorize rice husk [19]
3.2 Soil nutrient and Fertilizers

The nano confine materials used to increase the fertility of soil, high crop production, and minimum pollution are refereed as nano fertilizer. The use nano fertilizer improves the efficiency of fertilizer along with lesser requirement and bioaccumulation into the food chain. Some of the commercially available fertilizer are nano urea, the use nano urea increases the nitrogen use efficiency, since the use of conventional urea looses their 70% nitrogen contents during surface leaching [34]. In this regard, the improved solubility of urea further, improves at nano scale, thus for sustainable release several modifications are reported. For example, the urea was coated with bio-based epoxy comprised of nano-SiO$_2$ and organosilicon for improvement in properties like hydrophobicity. Water absorption, ammonium adsorption, and water contact angles. Thus, modified epoxy coated urea was enhanced urea release for longer time for 56 days with potential to use in modern agricultural practices [35].

The plants also need several micronutrients like zinc, iron, magnesium and born, however their normal salts either loss their retention capacity or absorption into plants body. These metal-based nanomaterials also work as anti-bacterial, antifungal, antiviral apart from micronutrients [36-37]. However, the novelty of materials at nano scale improves its both negative feature and several nano sized compound like iron oxide, zinc oxide, aluminum oxide, magnesium oxide and copper oxide are used a suitable micro nutrients [38-39]. The silver in nano sized are also in wheat crops to reduce phytotoxic nature of ozone as abiotic stress to improve the yield of crop. In general, the presence tropo-spheric ozone causes several damage including leaf injuries, which reduces the crop production. However, the anti-ageing feature of silver nano particles control negative feature of ozone exposure as well as improve the crop production [40-42]. Similarly, the presence of Zinc, in trace amounts is important and essential for optimum metabolic activities of plants and its deficiency reduces the production rate of crop [41-42]. In general the zinc manages the reactive oxygen species towards protection of plant cells against oxidative stresses as well
as formation of chlorophyll and carbohydrate. It is reported that wide range of soil are having deficiency, therefore the use nano sized zinc oxide as nano fertilizer improves the health of plants as well as productivity of crop. Magnesium oxide (MgO) is another important inorganic metal oxide with significant applications in agriculture chemical with antifungal and anti-microbial in nature. Further, the non-toxic nature of magnesium for human, frequently used in agriculture practices to inhibits pathogens and different microbes. Its working mechanism varies like coordination between with cell wall, enhanced formation of reactive oxygen species [43-46]. The other important point of nano fertilizer is formulation to ensure its quality availability for longer time. Currently, the blending of micronutrient and fertilizers are also used at nano scale to improve the functionality and effectiveness of nano technology. In this context, Kundu et al prepared iron oxide and urea nano composite as a novel fertilizer with improved nutrient utility and reduced environmental pollutions. The composite was used for seedlings of Oryza sativa L and checked for 14 days under hydroponic conditions and found significant up-regulation in photosynthetic efficiency as well as nitrogen metabolism due to better availability of both of nitrogen and iron [47]. In the above line the preparative mechanism for zinc and urea composite was shown in Figure 7 an along with its working impact on a wheat plant. The observation reveals the better growth of plants along with better agronomic performances [48].

![Figure 7. Preparation and use of zinc urea nanocomposite nano fertilizer on wheat plant [48].](image-url)
3.3 Sensing and monitoring

Different nanomaterials-based sensors are used in agricultural practice for monitoring of pH of soil, water contents, volatile ammonia and organic vapors. These parameters are important to grade soil nutrition index as well as improving the soil quality in the term of supplying additional fertilizer and nutrients. In this regards electrical, optical and gravimetric sensors are used for monitoring agrochemical and soil nutrients with precise sensing parameters [49-50]. In an example, Shukla et al has reported chemi-resistive sensors for monitoring of volatile ammonia from soil as nutrition index. The scheme of sensor along with basic components and parameters is shown below in Figure 8.

Figure 8. The nanocomposite based electrochemical sensor for volatile ammonia [51]

The basic principle and importance of ammonia sensing is based on adsorption of volatile ammonia after hydrolysis of urea from the adsorbed ammonia which changes the resistance of sensing layer and serve as a basic principle in ammonia sensing along effective sensing parameters i.e. response time, recovery time and sensitivity of sensing [51]. Similarly, pH monitoring is other significant parameters of soil to decide the fertility and selection of the crop for cultivation. In general, pH is sensed after measuring the induced color blue to red from acidic pH to basic pH or transition in resistance and current. Here, the use of nano particle controls the effective reactivity towards the induced changes because of interacting sites and surface area. Further, the integration pH responsiveness with remote control like Arduino helps the agriculture scientist to monitor the soil condition for policy making and mapping of soil pH Chajanovsky et al. have prepared a thin film of carbon nanotube and polyaniline using inverse polymerization using sonication. The obtained film was found suitable for electrochemical sensing of pH with high capacity due to synergistic effect of high surface area of CNTs and high electrical conductance of polyaniline. Thus, the developed property of composite was also found suitable for sensing of organic compounds
like aminophenol present in soil with high sensitivity [53]. Humidity is another important component of soil to insure the cultivation of crop. Several sensors are used for monitoring humidity using different nano materials like metal oxides, carbon nano structure and their polymer composites [54]. The nanostructure in humidity sensitive materials in the term of hydrophilicity and interactivity has improved the humidity sensitive nature, in this context several nano structured hydrogel, xerogel and composites are used efficient monitoring of precise humidity. In general the monitoring of humidity from soil is consist of different parts i.e. soil moisture metrics, in-situ soil moisture sensing methods, remote sensing methods and proximal in-field soil moisture monitoring. Thus, highly hydrophilic nano composite and hydrogels are most promising materials for humidity sensing with competitive sensing parameters. The commercially available temperature sensor is shown in Figure 9, which is an integral effect of heating probe and humidity sensors with sensitivity of 0.632 °C per 1% in the range of 5 to 41 %.

![Figure 9. The schematic of dual probe-based soil moisture sensor [55].](image-url)
The use of nanomaterials enhances the sensing parameters in the term of sensing range, sensitivity and response time [55]. In an example the use of reduced graphene oxide as sensing film has improved the sensing response of 60 -75 s along with stability for 5 months. The sensing principle of this kind of sensor is based on change in resistance due to after dissociative adsorption with water molecule, which is shown in Figure 10. It reveals that the first layer of H₂O adsorption is non ionizing due to covalent nature, while the subsequent layer of adsorption in ionizing nature and it yield hydronium and hydroxide ions. The generation of both ions increases conductance and decrease in resistance [56].

Figure 10. Chemi-resistive sensing mechanism for humidity over NiO and PANI nano composite [52]

Some more examples of nano technology based sensors along with brief properties for agriculture are listed in Table 2.
Table 2. Nanotechnology based sensors and their properties

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Materials</th>
<th>Type of Sensors</th>
<th>Analytes and sensing parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc oxide encapsulated polypyrrole</td>
<td>Electrochemical</td>
<td>Soil volatile ammonia, in the range of 1–100 ppm with sensitivity 0.4947 kΩ·ppm⁻¹ for 90 days.</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>ZnS quantum dots</td>
<td>Fluorescence</td>
<td>Urea, with dynamic limit 4 × 10⁻⁹ M to 4 × 10⁻³ M and low detection limit (&lt; 4 × 10⁻⁹ M)</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>Graphene quantum dots</td>
<td>Electrochemical low-cost sensors</td>
<td>Soil moisture in the range of water content 0% to 32% and response time 180 s</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>One-dimensional nanomaterial polyaniline</td>
<td>Electrochemical low-cost sensors</td>
<td>Ecotoxicity to earthworms, the soil enzyme activities i.e. sucrase, phosphatase, and protease.</td>
<td>59</td>
</tr>
<tr>
<td>5</td>
<td>Multiwall carbon nanotubes</td>
<td>Electrochemical</td>
<td>Chlorpyrifos in the concentration of 0.5 pM to 500 nM and detection limit of 0.16 pM</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>Graphitic carbon nitride</td>
<td>Square wave voltammetric technique</td>
<td>Amino-triazole and linuron in range of 3.0 × 10⁻⁷ to 4.5 × 10⁻⁵ M, and 1.2 × 10⁻⁷ to 3.0 × 10⁻⁴ M respectively</td>
<td>61</td>
</tr>
<tr>
<td>7</td>
<td>Polyaniline/nickel oxide</td>
<td>Electrocatalytic detection</td>
<td>epinephrine Very good performances achieved at a molecular level</td>
<td>62</td>
</tr>
<tr>
<td>8</td>
<td>Sodium alginate grafted polyaniline</td>
<td>Potentiometric</td>
<td>Mercury from 1.0 nM to 1000 μM with sensitivity of 0.25 mV μM⁻¹ cm⁻²</td>
<td>63</td>
</tr>
</tbody>
</table>

3.4 Crop protection and storage

The several nanomaterials are used as pesticides, insecticides, herbicides and preservatives to secure crops from microbial attack and environmental ageing. In this context different nanoparticles like metal oxides, metals, carbon nanostructure and polymer nano structure are used as agrochemicals like improved herbicides along with reduced negative effect [64]. In general, these agrochemical are two types one is exclusive in nano size, while other is hybrid of nano size. In an example Chitosan/tripolyphosphate nano particles were used to encapsulate nonselective widely used herbicides i.e paraquat. Thus, obtained nano formulation was found less toxic with conserve effectiveness for herbicidal treatment of
different plants [65]. Furthermore, the use of pristine pesticides in nano size improves the chemical efficiency of pesticides in term of reactivity and toxicity. In general, the use of traditional pesticides bears larger size, poor dispersibility, low stability and low biological activity along with low target utilization i.e. less than 30%. However the nano sized pesticide shows smaller size with high dispersibility and high target utilization, therefore the nano technology reduces the required amount of pesticides along with controls of the negative effect of pesticides towards environments. However, the improved dispersibility and scattering effects of nano sized pesticides also enters into the body of non-targeted organism and may cause unpredictable consequence as illustrated in Figure 11.

**Figure 11. Conclusive impact of nanosized pesticides**

Therefore, huge precaution is needed before commercializing a nano scale agrochemical like pesticides. Some representative nano sized agrochemicals along with their applications are listed in Table 3.
Table 3. Some different nano-sized agrochemicals and their applications in promoting agricultural sustainability.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Nano material as fertilizer</th>
<th>Nutrient</th>
<th>Applications</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydroxyapatite and urea</td>
<td>Nitrogen</td>
<td>35 % slower release of nitrogen for better supplements of N and K for leaves</td>
<td>66</td>
</tr>
<tr>
<td>2</td>
<td>Hybrid nanocomposite of Urea, hydroxyapatite and montmorillonite</td>
<td>Nitrogen</td>
<td>Sustainable release of urea for better crop yield</td>
<td>67</td>
</tr>
<tr>
<td>3</td>
<td>Nano sized zeolites</td>
<td>Phosphorous and Potassium</td>
<td>High increased release rate with better accumulation of P and K at optimum pH and moisture</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>Chitosan nanoparticle</td>
<td>N,P, and K</td>
<td>Better harvest and crop index with increase in root and shoot length</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>Nanosized calcium phosphate</td>
<td>N,P, and K</td>
<td>Better fertilization efficiency for précised agriculture with increased nitrogen efficiency</td>
<td>70, 71</td>
</tr>
<tr>
<td>6</td>
<td>Calcium nanoparticles</td>
<td>Calcium</td>
<td>Increased food nutrition quality for essential nutrition plant food</td>
<td>72</td>
</tr>
<tr>
<td>7</td>
<td>Zinc and Copper nanoparticles</td>
<td>Zn and Cu</td>
<td>Increase chlorophyll and carotenoid in the leaves Improved phenolic and flavonoid contents with better quality and quantity of basil</td>
<td>73</td>
</tr>
<tr>
<td>8</td>
<td>Nano sized zeolite</td>
<td>N,P, and K</td>
<td>Better vegetative growth, photosynthesis with increase in fresh and dry weight with phenols, tannins, flavonoids, and micro-elements</td>
<td>74</td>
</tr>
</tbody>
</table>
### Nanopesticides

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Nanomaterial</th>
<th>Nature</th>
<th>Target</th>
<th>Reference</th>
</tr>
</thead>
</table>
| 9      | Nanostructured alumina              | Nanoinsecticide | - Sitophilus oryzae  
- Oryzaephilussurinensis  
- Ceratitis capitate  
- Leaf-cutting ants | 75,76      |
| 10     | Nano silica                         | Nanoinsecticide | - Sitophilus oryzae  
- Rhizoperthadominica  
- Triboliumcastaneum  
- Oryzaephilussurinensis | 77         |
| 11     | Silver nanoparticles                 | Nano bactericides | - Xanthomonas axonopodis | 78         |
| 12     | Cu and Ag nanoparticles              | Fungicides    | Effective against Rhizoctonia solani, Phytophthora cactorum, Fistulina hepatica and Grifolafrondosa | 79         |
| 13     | Polycaprolactone nano capsules with atrazine | Herbicides   | Amaranthus viridis and Bidens pilosa | 80         |
| 14     | Essential oil Nanoencapsulation of savory (Satureja hortensis L.) essential oil | Herbicides   | Effective against Lycopersicon esculentum Mill and Amaranthus retroflexus L. | 81         |

### Conclusions and future prospects

The basic and novelty of nano particles has been described along with their applications in different agriculture practices. The adopted methods for synthesis are discussed along with secondary used tools for confinement effect and size particularly for geometry, physical and chemical properties. Furthermore, the role of different nano particles in valorization of agriculture wastes, nutrients, sensing and agrochemical are discussed along with effective illustration and schemes.

### References

https://doi.org/10.1016/j.scitotenv.2020.137778


https://doi.org/10.1039/D0EM00404A


https://doi.org/10.1039/D0MA00807A

https://doi.org/10.1016/j.nantod.2022.101389


https://doi.org/10.1007/s11356-014-2833-8


[23] N. Liu, K. Huo, M.T. McDowell, J. Zhao, Y. Cui, Rice husks as a sustainable source of nanostructured silicon for high performance Li-ion battery anodes. Sci Rep 3,(2013)1919. https://doi.org/10.1038/srep01919


