



Nanobiosensors: A Novel Approach in Precision Agriculture

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13.1 Introduction

A technology that can shape the modern agriculture for cost-efficient better production by providing the right amount of input at the right time is required because 60% of world population depends directly or indirectly on agriculture industry. As a result, agriculture is the building block of the economy. Conversely, excessive use of chemical fertilizer, pesticide, and herbicide, improper irrigation techniques, and environmental factors such as climatic changes escort to decline the share of sustainable agriculture fields (Panpatte et al. 2016). Due to various abiotic (drought, sunlight, humidity, climate, temperature, and pH etc) and biotic factors (insects, pest, diseases, weeds etc.), the agriculture industry cannot achieve the desired yield. It is inevitable to use technologies that will minimize yield loss in the agriculture industry. In this reference, biosensor tools which can help to know the minute details of the biological interactions at very small scale helps the farmer to achieve the maximum yield.

Nanobiosensors based on shrewd delivery systems could aid in the effective use of natural resources like water, nutrients, and agrochemicals in precision farming (Duhana et al. 2017). Therefore, having a significant role in recent technological developments, the nanotechnology can be used in remodeling the sustainable agriculture in order to meet the demands in a cost-effective way. Hence, this book chapter emphasizes the efficacy of nanobiosensors in precious agriculture to monitor the soil quality, pH, humidity, microbial load, etc. to boost productivity.

The probable benefits of nanobiosensors are enormous including intensification in agricultural productivity using nanoparticle-encapsulated fertilizers for sustained release of nutrients and water and insect pest management via formulations of nanomaterial-based pesticides and insecticides (Duhana et al. 2017). Nanoparticle-mediated recombinant DNA technology for the development of insect pest-resistant

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varieties in plants and use of nanomaterial for production of different kinds of biosensors plays central role in remote sensing devices which is obligatory for precision farming that is a boon for modern nanotechnology (Rai and Ingle 2012). Modern developments in biological techniques and instrumentation after using fluorescence tag to numerous nanocarriers like nanoparticles, nanowires, nanotubes, etc. have enhanced the sensitivity of biosensors. Utilization of nucleotides/aptamers, affibodies, molecule-imprinted polymers, and peptide arrays comprises boundless tools to formulate advanced biosensors. Merging of nanotechnology with biosensor systems boosted the diagnostic capability (Rajpoot 2017).

13.2 What Are Biosensors?

Biosensor is an analytical sensing device premeditated specifically for assessment of a biological interactions and assessing these interactions into a readable form with the help of a transduction and electromechanical elucidation. Bioreceptor, transducer, and the detector are three components of biosensors in terms of the conceptual and fundamental mode of operation. The sensing of biologically specific material such as antibodies, proteins, enzymes, immunological molecules, and so on is the central role of biosensors.

A first component bioreceptor serves as a template to detect specified component. Protein substrate and antibody antigen were the most appropriate examples of bioreceptors. To convert the interaction of bioanalyte and its equivalent bioreceptor into an electrical form is the function of the second component, transducer system. So, transducer principally converts one form of energy into another. The electrical signal from the transducer element was received and amplified appropriately to read and study the resultant response accurately by the third component, detector system (Fig. 13.1).

13.3 The Amalgamation of Nanotechnology with Biosensors: Nanobiosensors

A nanobiosensor is a modified biosensor, dense analytical device including a biologically sensitized element onto a physicochemical transducer with miniature structure. Nanomaterials are an exclusive gift of nanotechnology to the mankind having 1 to 100 nanometer dimension components. The size restraints of these components make them superior as most of their constituent atoms are located at their surface and had all dynamic physicochemical properties different from the similar materials at the bulk scale. A varied variety of constituents are used to make nanoparticles like ceramics, metal oxides, quantum dots, magnetic materials, semiconductor, lipids, polymers (synthetic or natural), emulsions, and dendrimers (Puoci et al. 2008).

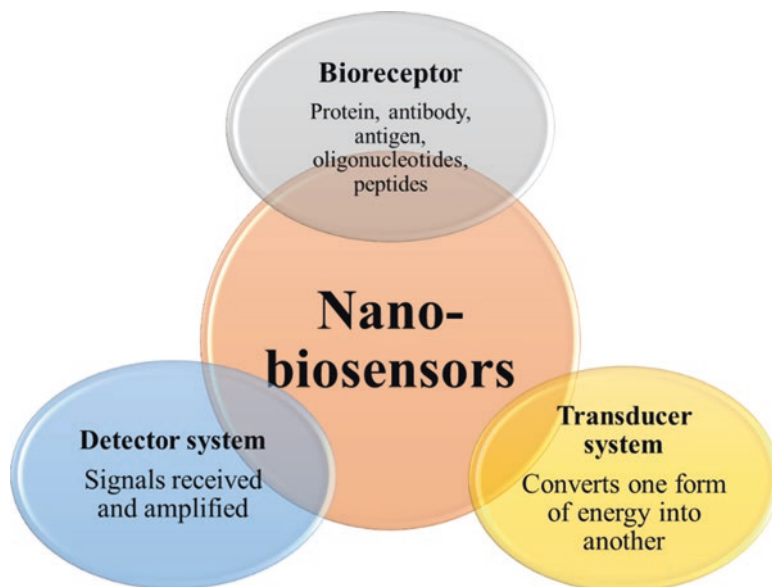


Fig. 13.1 Components of nanobiosensors

13.4 Applications of Nanobiosensors in Precision Agriculture

Nanobiosensors had highly versatile and multifunctional endless applications. Based on concept and definition, nanobiosensors had application in diagnosis of in vivo aspects related to health, toxicants, environmental monitoring of pollutants, heavy metal toxicity, physical aspects like humidity, presence of carcinogens, and various agricultural fields (Fig. 13.2).

Applications of nanobiosensors are as follows:

- (a) Nursing soil conditions (e.g., moisture, soil pH) for the monitoring herbicides, pesticides, insecticides, pathogens, fertilizers, and crop growth.
- (b) Food-borne contaminant detection.
- (c) Development of nanochips to identity preservation and tracking and delivery of fertilizers, herbicides, pesticides, and vaccines by nanocapsules (Miklicanina and Maksimovicb 2016).
- (d) Nanobiosensors a precious delivery system for effective use of natural resources (e.g., water), nutrients, and chemicals through smart farming.
- (e) Nanoparticles to deliver growth hormones or DNA to plants in controlled manner.
- (f) Sensor techniques to determine the heavy metals (e.g., Hg²⁺, As³⁺, Cu²⁺), antibiotics, secondary antibody, and residue analysis.

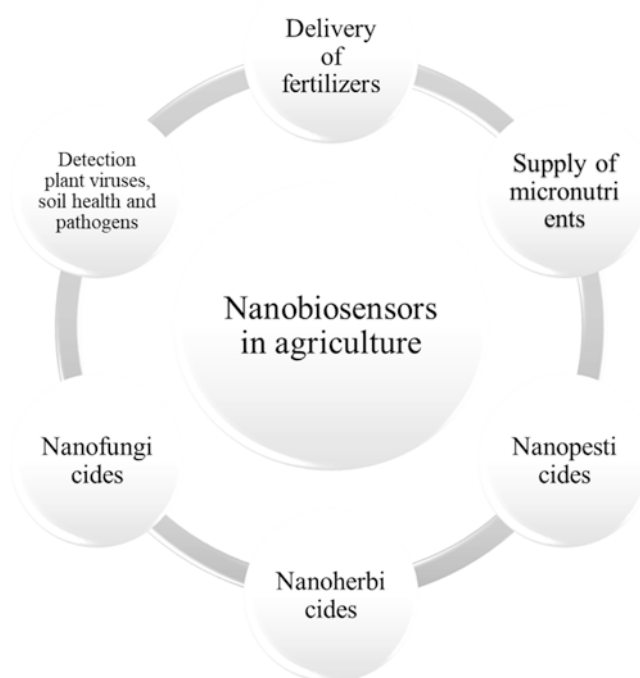


Fig. 13.2 Applications of nanobiosensors in agriculture

13.4.1 Delivery of Fertilizers

Ammonium salts, urea, and nitrate or phosphate compounds like huge amounts of fertilizers have central role in crop production; nevertheless these chemicals had detrimental effect on soil health, on soil microflora, and indirectly on animal and human health. Besides, the applied chemical fertilizers are run off and pollute the soil, water, and air. So, they are not available to plants and crops (Wilson et al. 2008). This problem can be solved by coating the chemical or biofertilizers with nanobiomaterials. In this regard, Liu et al. (2006) described that binding and coating of nano- and subnanocomposites from the fertilizer capsules can legalize the release of nutrients. Moreover, Jinghua (2004) exhibited that nano-composite consisting of N, P, K, mannose, amino acids, and micronutrients boost the uptake and use of nutrients in crops. Therefore, nanomaterials have probable contributions in slow release of fertilizers because nanobioparticles hold the components more strongly from the plant due to higher surface tension of nanobioparticles than conventional surfaces (Brady and Weil 1999). Moreover, larger particles got surface protection from nano-coating and binding (Santoso et al. 1995).

13.4.1.1 Chemical Fertilizers

Urea, diammonium phosphate (DAP), and single superphosphate (SSP) like chemical fertilizers are used in agriculture to meet the shortage of N, P, and K in the soil. After green revolution, the consumption of nitrogen fertilizer in the form of urea and diammonium phosphate has amplified manifold (29%). Nonetheless, superfluous nitrogen chemical fertilizer application for increase in food production causes global warming and an increase in temperature because it is responsible for 80% of the increase in atmospheric greenhouse gas N_2O (Park et al. 2012). But most part of the chemical fertilizers applied in field are vanished due to run-off or volatilized. It is assessed that about 40–70% of nitrogen, 80–90% of phosphorus, and 50–70% of potassium of the applied chemical fertilizers are vanished in the environment but cannot be absorbed by plants causing tremendous loss to the farmers' economy and environmental pollution as well (Trenkel 1997; Ombodi and Saigusa 2000). Since many nitrogen fertilizers have high solubility and potential vulnerability to leaching and denitrification (especially in the nitrate form), a wide range of slow-release fertilizers (SRFs) and controlled-release fertilizers (CRFs) have been produced using biopolymers (Shaviv 2000; Subramanian and Tarafdar 2011). The use of nanocoating and nano-binding of chemical fertilizers with nanosensors contributes to the slow release or controlled release of fertilizers. The stability due to the nanocoating and binding reduces the rate of dissolution of chemical fertilizer and permits slow, sustained release of chemical fertilizer. It is absorbed by plant roots more easily and efficiently. Recently, slow release of nanofertilizers is a precious approach to save fertilizer consumption in order to diminish environmental pollution (Wu and Liu 2008). Furthermore, it is identified that underneath nutrient constraint, crops secrete carbonaceous compounds into rhizosphere which helps the biotic mineralization of N and/or P from soil organic matter and P associated with soil inorganic colloids. Subsequently, the root exudates containing soil organic matter with N and P compounds can be considered as environmental signals and selected for the development of nanobiofertilizers (Al-Amin Sadek and Jayasuriya 2007; Sultan et al. 2009). Biodegradable polymeric chitosan, kaolin, and polymeric biocompatible nanoparticles have potential application in slow release of chemical NPK fertilizers (Corradini et al. 2010; Wilson et al. 2008).

Nanofertilizer-encapsulated nanosilica improves plant growth under high humidity and temperature stress as well as improves resistance to biotic stress because it binds to fungi and bacteria to form a binary films on the cell wall after absorption of nutrients (Wang et al. 2002). Moreover, silicon-based fertilizers increase biotic and abiotic stress resistance; subsequently silicon dioxide nanoparticles improve seedling growth and root development (Hutasoit et al. 2013). Controlled release of chemical compounds has been employed by zinc–aluminum-layered double-hydroxide nanocomposites which contribute as plant growth regulators. The non-toxic additives like TiO_2 or titanium may be used as additives to increase retention in fertilizers (Emadian 2017). Polymethacrylic acid (PMAA) chitosan nanoparticles for NPK fertilizer preparation have been reported. The chitosan–polymethacrylic acid (CS-PMAA) colloidal suspension was found to be more stable with the

addition of nitrogen, potassium, and phosphorus, because of the higher anion charge from the calcium phosphate than the anion charges from the potassium chloride and urea (Hasaneen et al. 2014). Emadian (2017) reported that the CS-PMAA combined with 500 ppm of nitrogen has higher stability compared with that of phosphorus. Moreover, the adsorbents like montmorillonite, zeolite, bentonite nanoclays, and halloysite were used to develop nitrogen fertilizers with controlled-release characteristics reported by Sharmila in 2010 (Table 13.1).

13.4.1.2 Biofertilizers

Mycorrhizae, *Rhizobium*, *Azotobacter*, *Azospirillum*, and blue-green algae and phosphate-solubilizing bacteria like *Pseudomonas* and *Bacillus* are included in biofertilizers which are beneficial living microorganisms (Wu et al. 2005). These plant growth-promoting microorganisms improve plant growth by fixing atmospheric nitrogen, solubilizing or mobilizing phosphorous and potash, producing siderophores, producing plant growth hormones, and relieving stress by producing ACC deaminase enzyme as well as convert organic matter into simple compounds that provide essential nutrients to plants, improve soil fertility, maintain the natural habitat of the soil, and increase crop yield. Short shelf life, temperature sensitivity, and storage desiccation are the crucial drawbacks in biofertilizer technology. Polymeric nanoparticles for coating of biofertilizer preparations are utilized in formulations which proved to be resistant to desiccation. Water-in-oil emulsion is a novel

Table 13.1 Properties and applications of nanobiosensors in fertilizer technology

Sr. no.	Properties of nanosensor fertilizers technologies	Applications	References
1.	Controlled-release formulation	Precisely control the release speed of nutrients to match the uptake pattern of crop	Shaviv (2000) and Subramanian and Tarafdar (2011)
2.	Solubility and dispersion for mineral micronutrients	Nanocoating and nano-binding improve solubility and dispersion of insoluble nutrients in soil, reduce soil absorption, and increase the bioavailability	Peteu et al. (2010) and Ghafariyan et al. (2013)
3.	Nutrient uptake efficiency	Save fertilizer resources by increased fertilizer use efficiency and uptake ratio of the soil nutrients	Corradini et al. (2010) and Wilson et al. (2008)
4.	Controlled-release modes	Both release rate and release pattern of nutrients for water-soluble fertilizers precisely controlled through encapsulation of semipermeable membranes coated by resin-polymer, waxes, and sulfur	Sharmila (2010)
5.	Effective duration of nutrient release	Extend effective duration of nutrient supply of fertilizers into soil	Wu and Liu (2008)
6.	Loss rate of fertilizer nutrients	Reduce loss rate of fertilizer nutrients into soil by runoff and leaching	Hasaneen et al. (2014) and Emadian (2017)

potential technique for storage and distribution of microorganisms through liquid formulations (Vandergheynst et al. 2006). It improves cell growth, cell proliferation, viability, and growth kinetics by addition of biofertilizers to the oil or aqueous phases. It downs the evaporation of water due to oil that traps the water around the cells of microorganism. Vandergheynst et al. (2007) reported that the hydrophobic silica nanoparticles improve cell viability by condensing the oil phase through storage and reduce cell sedimentation. Gnanamangai et al. (2012) described the effective procedure for the development of silver and gold nanoparticles from various categories of microbes like bacteria, fungi, and actinomycetes isolated from the tea fields, which can efficiently work as biocontrol/biofertilizer agent in field to control various diseases individually and in combinations with other microbes. Nanobiosensor-based biofertilizers like nitrogen fixing, phosphate solubilizing, and potash mobilizing developed from silver and gold nanoparticles to overcome the limited availability of land and water resources are very effective (Dikshit et al. 2013; Mishra et al. 2014). The nanobiosensors with biofertilizers such as *Pseudomonas fluorescens*, *Bacillus subtilis*, *Rhizobium* sp., *Azotobacter* sp., *Azospirillum* sp., and *Paenibacillus elgii* promote the growth of crop plants under in vitro conditions (Shukla et al. 2015).

13.4.2 Supply of Micronutrient

Soil is the storehouse from which plants receive macronutrients (phosphorus, potassium, sulfur, calcium, magnesium, nitrogen) and micronutrients (boron, copper, iron, manganese, molybdenum, nickel, selenium, chloride, cobalt, and zinc) (Goron and Raizada 2014). Micronutrients are important for the plant growth and development is a well-established fact. After the green revolution and new farming practices the crop yields are increased, but essential micronutrients for plant growth and development from soil are decreased (Alloway 2008). Therefore, there is a need to improve the investigative tests for micronutrients which are inexpensive and sensitive and provide three-dimensional and chronological information regarding bioavailable nutrient pool in plants and soil (Goron and Raizada 2014).

Nanoformulations containing micronutrients can be applied by foliar application on plants or soil application to make available for uptake by roots to enhance soil health and vigor (Petu et al. 2010). Regarding micronutrients, soils with high pH and calcareous soil had the iron deficiency in plants' growth. Nanobiosensor technology for the development of iron compound formulations can overcome this significant issue. Iron nanoformulations have positive effect on various crops such as increase in chlorophyll contents and reduction of chlorotic symptoms of iron deficiency in soybean (Ghafariyan et al. 2013), growth, yield and quality spike weight, 1000 grain weight, biologic yield, grain yield, and grain protein content of wheat (Bakhtiari et al. 2015) and number of pods per plant (47%), weight of 1000 seeds (7%), the iron content in leaves (34%), and chlorophyll content (10%) over the controls in black-eyed peas (Delfani et al. 2014). Similarly, manganese nanoparticles

illustrated the enhancement of growth and yield of mung bean (*Vigna radiata*) photosynthesis (Pradhan et al. 2013), and zinc oxide nanoparticles had improved growth of mung bean and chickpea (*Cicer arietinum*) seedlings at low concentrations (Mahajan et al. 2011).

13.4.3 Nanopesticides

Formulations with active ingredient of pesticide properties developed from engineered structure are defined as nanopesticides. These nanoformulations provide controlled release and slow degradation of active component for a long time which make them less lethal as well as environmentally safe as related to chemical pesticide. Kah and Hofmann (2014) presented detailed report in contest to development of nanopesticides like nanospheres, nanoemulsion, nanocapsulated formulations, nanogel, and metal oxide nanoparticles which had boundless potentials for management and control of insect pest in modern agriculture. The polyethylene glycol-coated nanoparticles of garlic essential oil against *Tribolium castaneum* (red flour beetle) resulted in amplification due to slow and controlled release of active components (Yang et al. 2009). Goswami et al. (2010) demonstrated the different types of nanoparticles, viz., zinc oxide, silver, aluminum oxide, titanium dioxide etc. to control rice weevil (caused by *Sitophilus oryzae*) and grasserie disease in silkworm (caused by *Bombyx mori* and baculovirus) were used (Table 13.2).

Furthermore, pesticides in agriculture elevated public concern regarding the safety of food products. Organophosphorus (OP) and carbamates (C) are major chemical pesticides comprising ~40% of the world market (Singh and Walker 2006;

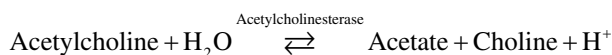
Table 13.2 Nanobiosensor used as nanopesticides

S. no.	Type	Applications	References
1.	Polyethylene glycol-coated nanoparticles	Controlled release of active components	Yang et al. (2009) and Kitherian (2016)
2.	Chitosan nanoparticles	Slow degradation of active component	Chandra et al. (2013)
3.	CdS, nano-ag, and nano-TiO ₂	Efficient delivery of pesticides, fertilizers, and other agrochemicals	Chakravarthy et al. (2012)
4.	Silver and zinc nanoparticles	Act against <i>Aphis nerii</i> Boyer De Fonscolombe and against Asian armyworm, <i>S. litura</i> , and castor semilooper, <i>Achaea janata</i> L. (Lepidoptera: Noctuidae)	Rouhani et al. (2012a) and Yasur and Rani (2015)
5.	Polystyrene-coated magnetic nanoparticles	Monitoring and detection of pesticides from agricultural products and food samples	Hongshun (2018) and Valdés et al. (2009) and Pérez-López and Merkoçi (2011)
6.	Acetylcholinesterase nanobiosensor	Detection of pesticide residue	Vimala et al. (2016)

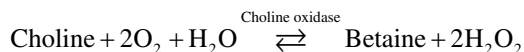
Kumar et al. 2010) which inhibits the acetylcholinesterase (AChE) enzyme that acts as hydrolysis of neurotransmitter acetylcholine (Andrescu and Marty 2006; Pope 1999). The expensive, time-consuming techniques including chromatographic techniques (GC and HPLC) and coupled chromatographic-spectrometric procedures such as GC-MS and HPLC-MS are recently used for monitoring the pesticide contaminants. Therefore, sensitive and selective smart nanobiosensor techniques could improve detection and monitoring of pesticide residue from crop products and food samples (Valdés et al. 2009; Pérez-López and Merkoçi 2011).

Vimala et al. (2016) explained the development of enzyme-based electrochemical biosensors by combining enzymatic reactions with electrochemical methods. Amperometric acetylcholinesterase (AChE) biosensors inhibit the AChE applied for detection of pesticides.

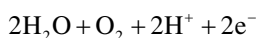
Hydrolysis of acetylcholine:



Oxidation of choline:



Electrolysis of H₂O₂:



Pesticide became more toxic during the degradation than parent compounds and persists in soil and plant parts for long time. These organic toxins accumulate in animal and human bodies directly or indirectly through bioaccumulation or in drinking water. It directly affects the essential acetylcholinesterase for the central nervous system in humans (Fig. 13.3).

13.4.4 Nanoherbicides

Besides nutrient management and insect pest, the weeds are the foremost threat in agriculture which decline the yield. These can be eradicated by conventional method like hand weeding, but these are time-consuming, require labor force, and are not economical means. Recently, many chemical herbicides are available which affect the crop plants and responsible for the environmental pollution and affect soil

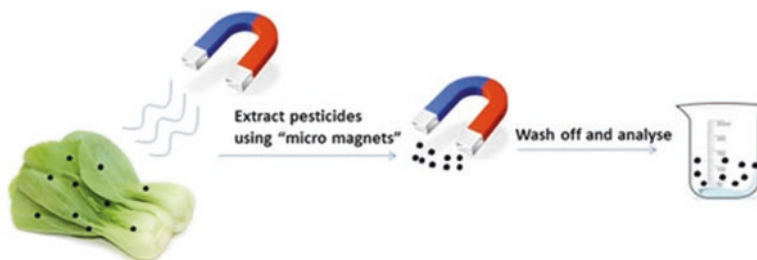


Fig. 13.3 Detection of pesticide residue from vegetables and food samples. (Source: www.nanowerk.com/nanotechnology-news/newsid=49463.php, Retrieved on 19th Dec, 2018)

fertility. Therefore, the nanoherbicides proved to be effective and economical alternative for weed control without the harmful residue issue in soil and environment (Pérez-de-Luque and Rubiales 2009). To mitigate the problem of toxicity and environmental pollutants, the controlled-release systems using nanobiosensors are recently increased, and they also increase herbicide efficiency (Clemente et al. 2014).

Based on the above explanation, monitoring and detecting the presence of chemical herbicides as pollutants is critical for environmental safety. Nanobiosensors through enzymatic reaction can detect minute quantities of a specific element. The functionalized ZnS quantum dots (ZnS-QDs) proved as inexpensive, simple, and rapid nano quantum dots and measurement of various herbicides. It can be characterized by transmission electron microscopy (TEM), x-ray diffraction (XRD), energy-dispersive x-ray (EDX) analysis, Fourier transform infrared (FT-IR) spectroscopy, and ultraviolet-visible (UV-vis) and photoluminescence (PL) spectroscopies (Masteri-Farahani et al. 2018). The new generation of lipid membrane biosensors has the potential to analyze the analyte-tailored types of responses (Nikoleli et al. 2018). Clemente et al. (2014) showed that when herbicides are encapsulated in the poly(ϵ -caprolactone) nanocapsules, it may be resulted in minor noxiousness to the alga (*Pseudokirchneriella subcapitata*) and higher toxic to the microcrustacean (*Daphnia similis*) as related to herbicide alone.

13.4.5 Nanofungicides

Major causes in agricultural loss include another factor, i.e., fungal disease, and to mitigate this problem, various chemical fungicides are available in market in recent era, and these had many adverse effects on human beings and environment.

Abd-Elsalam and Alghuthaymi (2015) showed that the biosynthesized Ag nanoparticles (bsAgNPs) had strong inhibitory effects against fungal diseases. They further explained that the green bsAgNPs had strong activity against *Bipolaris sorokiniana* and can effectively control its infection in wheat plants. The synthetic fungicides are replaced by biosynthetic nanoparticles which are generally recognized as safe (GRAS) in recent years. Nanobiocide a product prepared by mixing several

bio-based chemicals was reported to eliminate fungus *Magnaporthe grisea*, the causal agent of rice blast disease (Gogoi et al. 2009). Chitosan and Cu–chitosan nanoparticles demonstrated their consistent size and stability, which contribute for the in vitro higher antifungal activity against *A. alternata*, *M. phaseolina*, and *R. solani*. *A. alternata* spores are strongly inhibited by Cu–chitosan nanoparticles, and the chitosan–saponin nanoparticles were found poor in antifungal activity (Abd-Elsalam and Alghuthaymi 2015). In controlling the pathogen, nanoparticle-mediated gene transfer technology is very useful (Fig. 13.4).

The emerging nanosized fungicides are recently synthesized by using different microbial cells like *Fusarium*, *Aspergillus*, *Verticillium*, and *Penicillium* (Abd-Elsalam and Alghuthaymi et al. 2015).

13.4.6 Detection of Plant Viruses, Pesticides, Soil Health componets, and Pathogens

Da Silva et al. (2013) reported that the nanobiosensors constructed on atomic force microscopy tip functionalized with the acetolactate synthase enzyme were detected for herbicide metsulfuronmethyl (an acetolactate synthase inhibitor) through the procurement of force curves. Rapid detection of bacteria and viruses with detailed quantification was made possible due to the bionanosensors which increase the food security (Otlés and Yalcin 2010). An innovative acetylcholinesterase (AChE) biosensor was developed based on multilayer films containing multiwalled carbon

Fig. 13.4 Bionanofactory for synthesis of nanobiofungicides.
(Source: Abd-Elsalam and Alghuthaymi et al. 2015)



nanotubes (MWCNTs), chitosan (CS), and AChE liposome bioreactor (ALB) for detection of organophosphate pesticides (Yan et al. 2013). Xiong et al. (2018) published the brief review on achievements and problems in enzyme-functionalized nanostructure biosensor organophosphorus pesticide detection.

Similarly Sun et al. in 2013 developed the highly sensitive acetylcholinesterase biosensor modified with hollow gold nanospheres for the detection of $0.06 \mu\text{g}/\text{dm}^3$ for chlorpyrifos and $0.08 \mu\text{g}/\text{dm}^3$ for carbofuran. Moreover, it presented a good stability and reproducibility also suitable for detection of trace pesticide residues in vegetables and fruits. Nano-smart dust (the use of tiny wireless sensors and transponders) and gas sensors were used to quickly evaluate levels of environmental pollution. Atomic force spectroscopy became more effective in detecting enzyme-inhibiting herbicides. A nanobiosensor based on an atomic force microscopy tip functionalized with the acetolactate synthase enzyme was successfully detected for the herbicide metsulfuron-methyl (an acetolactate synthase inhibitor) through the acquisition of force curves. Bionanosensors also allow the more quantification and rapid detection of bacteria and viruses, thereby increasing the safety of the food for the customer. Electrochemically functionalized single-walled carbon nanotube (SWCNT)-based nanosensors with metal/metal oxide nanoparticles or nanotubes for gases, viz., ammonia, nitrogen oxides, hydrogen sulfide, sulfur dioxide, and volatile organics, have potential application in monitoring agricultural pollutants (Sekhon 2014). Farrell et al. in 2013 published that Nanotechnology Signature Initiative entitled “Nanotechnology for Sensors and Sensors for Nanotechnology: Improving and Protecting Health, Safety, and the Environment.” They also showed that the portable nanodevices can rapidly detect insects, diseases, pathogens, chemicals, and contaminants.

Biosensor design showed good compatibility between membranes and enzymes without a change of the conformation of the enzyme molecule, and binding always takes place outside the enzyme active centers (Sekhon 2014).

13.5 Types of Nanobiosensors Based on Nanomaterials

The nanobiosensor classification is very tedious and diverse because of the nature of nanomaterial used and sensing mechanism applied. Mostly the nanobiosensors were classified based on nanomaterial used for enhancement of the sensing mechanism. For instance, nanobiosensors may include metallic, magnetic, nanotube, or quantum dot-based nanomaterial for development and similarly classified accordingly (Fig. 13.5).

13.5.1 Acoustic Wave Biosensors

The variety of biological and chemical analytes were detected using resonant and acoustic wave devices for several decades, and researchers were engaged in development of the sensing devices. These biosensor devices operated by coupling the analyte adsorption as a modulation in the physical properties of the acoustic wave (e.g., resonant frequency, acoustic velocity, dissipation) that can then be correlated

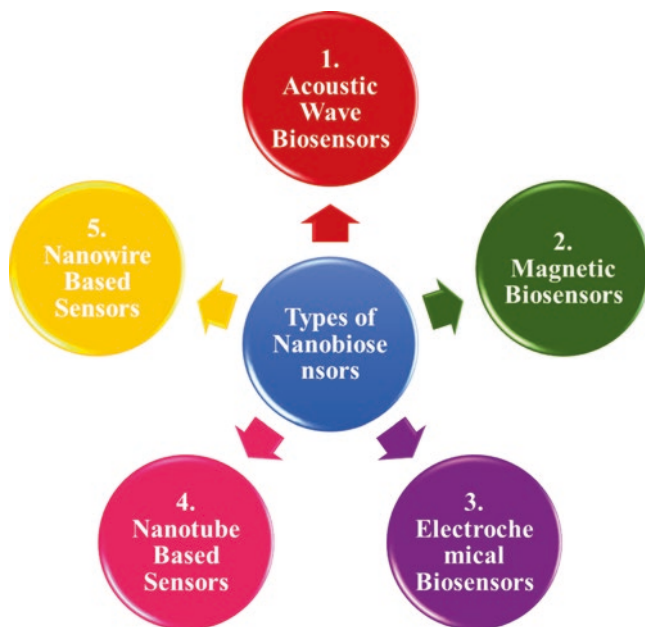


Fig. 13.5 Types of nanobiosensors based on nanomaterials used

with the amount of adsorbed analyte (Fogel et al. 2016). The precision of the detection of biological agents can be improved through the acoustic wave biosensors. Piezoelectric materials (crystalline solids lacking a center of inversion symmetry and representing strong coupling between mechanical strain and electrical polarization) were frequently employed in acoustic sensors to generate acoustic waves in solid materials using properly tailored electric fields and to detect the acoustic waves by the charge generated due to the induced mechanical deformation. The mass-based variant of these sensors involves the conjugation of antibody-modified sol particles which bind themselves on the electrode surface that has been complexed with the particles of analyte conjugated in a manner that antibody molecules are immobilized over the electrode surface. The large mass of bound sol particles of the antibody results in a change in the vibrational frequency of the quartz-based sensing platform, and this change acts as the basis of detection (Su et al. 2000; Liu et al. 2004). Acoustic wave device technologies have the potential to form significant segment of the biosensor market, due to their low operating cost, sensor compactness, real-time data responses, and high sensitivity.

13.5.2 Magnetic Biosensors

Magnetic relaxation switching (MRSw) assay-based nanosensors respond to the variations of transverse relaxation time (T_2) of water molecules caused due to the

analyte-induced aggregation and disaggregation of magnetic nanoparticles (MNPs). The same approach has been extensively used for the detections of various substrates like heavy metal ions, proteins, nucleic acids, organic pollutants, bacteria and viruses, and specific cells (Zhang et al. 2017).

Tanya et al. in 2013 reported that the magnetotactic bacteria, which are able to produce magnetic nanocrystals having uniform shapes and sizes at physiological conditions, serve as a motivation source of biological macromolecules used for the biomimetic synthesis of a diversity of magnetic nanomaterials. As compared to conventional biodetection devices, the novel magnetic nanobiosensors have become a more sensitive, powerful, and cost-effective approach.

13.5.3 Electrochemical Biosensors

Electrochemical biosensors basically work on electrical means to analyze the biochemical reactions which made up of metallic nanoparticles. The biomolecules easily and efficiently carry out chemical reactions with the help of metallic nanoparticles which significantly immobilize the reactants. Chen and his coworkers in 2008 explained that the significant role of acetylcholinesterase (AChE)-based electrochemical sensors for the environmental pesticide detection. They introduced the multiwalled carbon nanotubes (MWNTs) and showed its dual enrichment roles. First is the increased surface area due to MWNTs loaded on glassy carbon (GC) electrodes which assist the electrochemical polymerization of Prussian blue (PB), a redox mediator for the electrochemical oxidation of the enzymatic product, thiocholine (TCh). Second, MWNTs increase the enzymatic activity of AChE, as demonstrated by the decreased Michaelis–Menten constant (K_m). Electrochemical biosensors analytical method provides reliable, sensitive, less time consuming method in which pretreatment steps may be reduced and integrated with reverence to other analytical methods (Bakirhan et al. 2018). In a momentous study by Xu et al. (2003), they analyzed the electrochemistry of enzyme systems containing horse reddish peroxidase which is immobilized on gold electrodes overloaded with nanoparticles of carbon. They showed that the horse reddish peroxidase has faster amperometric response and superior electrocatalytic reduction ability which resulted in the biosensor development having enhanced sensitivity and much lower detection limit as compared to the one without using nanoparticles. Similarly, nano-sized semiconductor crystals may be used to improve the efficiency of photochemical reactions and precursors to design novel photo-electrochemical systems. In this regard, Curri et al. (2002) have utilized immobilized nanocrystalline CdS having self-assembly approach to develop an enzymatic detection system based on immobilized formaldehyde dehydrogenase onto the gold electrodes in order to carry out the catalytic oxidation of formaldehyde. Similarly, in this decade, in several other studies, metal-based nanoparticles have been used for coupling themselves with biological probes and then carry out useful detection of the specific molecules from a mixture. Moreover, Tan et al. (2016) explained that the numerous signal intensification stratagems in conjunction with microfabrication technology have been

extensively studied and have resulted in significant improvements in the sensitivity and multiplexing capability of electrochemical nucleic acid biosensors. In one study, explained that the electrochemical biosensing of DNA hybridization is not only exceptionally competent for meeting the size, cost, and power requirements of distributed genetic testing but also proposes a smart route for interfacing at the molecular level in the DNA recognition and signal transduction elements.

13.5.4 Nanotube-Based Sensors

Carbon nanotubes have recently been used widespread as nanomaterials in the world of material science and optoelectronic applications. These materials are discovered in 1990s and thereafter attracted awareness worldwide because of their extraordinary properties, the most dynamic of which are the electronic conductivity, flexible physical geometric features, and the ever dynamic physicochemical properties ranging from high aspect ratios to very good functionalization abilities along with having high mechanical strength and folding abilities. The single-walled nanotubes and multiwalled nanotubes are utilized for the enhanced and better performance due to their unusual features. Carbon nanotubes (CNTs) may assist as scaffolds for immobilization of biomolecules at their surface and combine several exceptional chemical, electrical, physical, and optical characteristic properties that confer this materials for the transduction of signals linked with the appreciation of analytes, metabolites, or disease biomarkers (Tilmaçiu and Morris 2015). Carbon nanotubes (CNTs) are developed by a hollow cylinder of an exclusive carbon sheet with a single-walled carbon nanotube (SWCNT) or concentric carbon sheets of different diameters forming multiwalled carbon nanotubes (MWCNTs) with sp^2 bonding (Sagadevan and Periasamy 2014). Furthermore, chemoelectroluminescence effect has been enhanced by coupling CNTs to the sensing molecules of a sensor by better conductance of charge transporters and controlling the essential stream characteristics. This explains the functionalization prospective of carbon nanotubes and their rapid friendliness for being coupled with biomolecules like DNA, proteins, oligonucleotide probes for their corresponding benefits.

13.5.5 Nanowire-Based Sensors

Nanowire biosensors contain nanowires coated by biological molecules such as polypeptides, fibrin proteins, DNA molecules, and filamentous bacteriophages. Bionanowires are cylindrical arrangements with one-dimensional fibril-like nanostructure, with the lengths in the order of few micrometers to centimeters and diameter constrained to the nanorange. The surface properties of these nanowires can be easily altered, so the nanowires can be adorned with virtually any potential chemical or biological molecular recognition unit, creating the wires themselves analyte independent. The nanomaterials transduce the chemical binding on their surface into a modification in conductance of the nanowire in an enormously sensitive,

real-time and quantifiable fashion. The motion of charge carriers in nanowires is significantly improved and very diverse as compared to bulk materials for the detection of biological materials. The group of two scientists named Cui et al. has reported the concert of biosensors based on silicon nanowires doped with boron and utilized them for the detection of biological and chemical species. Semiconductor nanowires have been exploited in detail and have also been used for coupling a number of biomolecules for identifying their specifically linked substrates. In this study, silicon nanowires coated with biotin have been used for the detection and isolation of streptavidin molecules from a mixture. The nanowires make them ideal elements due to their small size and capability to be used for pathogen biodetection and many other real-time analysis of a wide range of biological and chemical species, thus vastly improvising the current precisions of presently used in vivo diagnostic procedures to function in the smallest environments within the living cells. Assembly of microfabricated gold interdigitated microelectrodes and polypyrrole (Ppy) nanowires was extensively used for the microbial spore detection showing good linear correlation ($r^2 = 0.992$) for low spore concentrations ranging from 1 to 100 CFU (colony-forming units)/mL, a concentration. Also the Ppy nanowires proved to be the worthy platform for the detection and quantification of large molecules and biocomponents even at low concentrations (García-Aljaro et al. 2010). Silicon nanowires (SiNWs) as sensitive units invented by self-assembly system (vapor–liquid–solid mechanism), companionable with complementary metal oxide semiconductor (CMOS) silicon technology for reduction and integration of lab-on-a-chip systems, were developed as simple and low-cost fabrication technology bacteria sensors which favor bacteria hanging and thus increase the sensitivity for detection of bacteria (Borgne et al. 2017). Moreover, Patolsky et al. (2006) suggested the potential of nanowire sensors that transduce chemical and biological binding events into electronic and digital signals for a highly sophisticated interface between nanoelectronic and biological information processing systems. In another very closely study, Cullum et al. (2000) have reported the use of ZnO nanowires coated over the gold electrodes using amperometric responses for detection of hydrazine. They also suggested the extraordinary sensitivity, low detection limit, and far lower response times than those reported in the conventionally used sensor systems. Nanowires are very versatile in their performance and are significantly better than nanotubes in two major ways. First, they allow a range of modifications in their design by control of operational parameters during their synthesis. Second, they possess a lot much more scope for the development of functionalized assemblies by virtue of the existence of compatible materials on their surfaces.

Overall, the nanomaterial hybrids established after utilizing nanostructures (i.e., nanowires, nanoparticles, carbon nanotubes, nanorods, etc.) reveal combined characteristics of the specific nanomaterials. In above manner, nanosized materials have been evidenced to be extremely thriving for enhancing the sensing technology and have improved the diagnostic and detection procedures by leaps and bounds. The biosensing mechanism has been revolutionized by the nanosized elements and through the faster, low operating cost, sensor compactness, real-time data responses and high sensitivity, and quantifiable detection and diagnostic protocols. There are

numerous nanomaterials as mentioned in above description that have been used for the biosensing applications. These abovementioned nanomaterials were successfully utilized for the detection of antibody, pesticides, pathogens, viruses, as well as molecular level in the DNA recognition and signal transduction elements. Acoustic wave biosensors generally operated by coupling the analyte adsorption as a modulation in the physical properties of the acoustic wave (e.g., resonant frequency, acoustic velocity, dissipation) that can then be correlated with the amount of adsorbed analyte to detect the antibody. Similarly, magnetic biosensors are used for the detections of various substrates like heavy metal ions, proteins, nucleic acids, organic pollutants, bacteria and viruses, and specific cells. The smartness of the nanobiosensor is increased due to the coupling of piezoelectric and cantilever systems. These techniques have yielded highly sensitive detections that can be monitored easily by thermochromic, photochromic, and electrochromic mechanisms.

13.6 Conclusions

In the 1960s, the first biosensor was introduced. It was designated the solicitation of enzyme-based bioelectrodes for their biocatalytic action. Afterward several kinds of biosensors are considered and utilized that include enzyme-based biosensor, immunosensors, cell- or tissue-based biosensor, nucleic acid biosensors, and thermal and piezoelectric biosensors. Enzyme-based biosensors are being established using immobilization techniques, i.e., covalent or ionic bonding and adsorption of enzymes via van der Waals forces by exploiting enzymes such as oxidoreductases, amino oxidases, polyphenol oxidases, and peroxidases. Antibody-based biosensors had additional affinity in the direction of particular antigens, viz., the antibodies bind specifically to the toxins or pathogens or interact with different components of the immune system of the host. The applications of nanobiosensors are very diverse and vast which includes different areas like virology, ligand fishing, cell biology, cell adhesion, epitope mapping, bacteriology, nucleotide–nucleotide binding, molecular engineering, nucleotide–protein, enzyme mechanisms, and signal transduction.

The biosensors are developed based on various novel techniques like magnetic, optical, fluorescence-based, quantum dots, electrochemical, nanowire based, electromechanical, and nanotube based which are modern transducing methods. All the research areas now are fulfilled by these novel biosensors like novel drug discovery, agriculture, food technology, biomedicine, food safety processing, security, residue analysis laboratories, environmental monitoring, and defense. Thus all these inventions are of immense importance due to accurate and sensitive biosensors which include the improved sensitivity, the possibility of developing label-free detection methods, less time, high-throughput screening, and real-time analysis. Recently it is observed that the merging of nanotechnology with biosensors has great practical importance in the field of agriculture to detect the pesticides, pathogens, viruses, as well as controlled release of chemicals and fertilizers. Furthermore, these nanobiosensors are greatly utilized to monitor the residue

analysis in fruits and agricultural produce. In the future the special attention should be given to the exact role of biosensors during the controlled fertilizer and pesticide release as well as the side effects of all these sensors in plants and fruits.

13.7 Limitations and Future Prospective

Despite the developments of nanobiosensor and implications in all fields, the applications of nanobiosensors in agricultural and allied fields are still not exploited well. Therefore, to exploit the advances of nanobiosensors in agricultural field, it is very essential to understand the interaction between plants and nanobiosensors as well as their phytotoxic effects. Overall, the nanobiosensors have great applications in agriculture for nanobiofertilizer production, controlled release of fertilizers, pesticides, nanoherbicides, and detection of pesticide residue and pathogens like viruses, bacteria, fungus, etc. Nonetheless the more emphasis is required on suitable nanomaterials for nanobiosensor development and methods of applications. Furthermore, the role of biological elements and nanomaterials like enzymes, proteins, tissues, and nucleic acids for the nanobiosensor development is very crucial so that residue issues in agriculture produce and food products will be minimized. Therefore, the special attention should be given toward the nanobiosensor development from biological elements.

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