Sensors and Biosensors for Environment Contaminants

Heba M. Mohamed

Contents

1 Introduction: Sensors/Biosensors as Green Analytical Tools

Many years' worth of effort has been dedicated by researchers to investigate and develop technologies toward both detection and reduction of the environmental impact of hazardous compounds. Electrochemical sensors prove to have several potentialities to detect widespread environmental pollutants like pesticides, heavy metals, polycyclic aromatic hydrocarbons, and toxins, and other emerging contaminants including gasoline additives, pharmaceuticals, hormones, personal

---

H. M. Mohamed (✉)
Faculty of Pharmacy, Cairo University, Cairo, Egypt

Higher Colleges of Technology, Abu Dhabi, UAE

Inamuddin, A. M. Asiri (eds.), *Nanosensor Technologies for Environmental Monitoring*, Nanotechnology in the Life Sciences,
https://doi.org/10.1007/978-3-030-45116-5_6

care products, endocrine-disrupting agents, organometallic compounds, disinfection by-products, plasticizers, perfluorinated compounds, and surfactants that are considered a massive threat for living things and ecosystems. Nowadays, monitoring the environment for various pollutants has become a fundamental factor to attain sustainability goals (Azmuddin et al. 2017). The principles of sustainable and green chemistry have a great focus on new eco-friendly synthetic paths and promoting development of analytical processes for real-time and in situ monitoring of perilous substances. Pioneering green technologies and tools are substantial to diminish or abolish the usage or production of perilous materials and minimize energy consumption. In this context, sensors/biosensors are expansively recognized to be highly useful for identification, monitoring, and analysis of various substances owing to their ease of use, simplicity of construction, portability, sustainability, and considerably cost-effective development (Kimmel et al. 2011).

The application of nano-sensors/biosensors in environmental monitoring and analysis has become increasingly imperative, and many researchers show a particular interest on the different types of fabricated structure encompassing those made by self-assembly, which can be adapted for monitoring of chemical processes (Riu et al. 2006).

In the last decades, novel and green synthesis procedures for nanomaterials and miniaturization approaches used for fabrication of sensors and biosensors to improve their eco-friendliness level toward more sustainability have emerged as promising tools for environmental monitoring and prompt warning. Green synthesis is essential to evade hazardous by-product production by using sustainable, reliable, and environment-friendly synthesis processes (Singh et al. 2018). Eco-friendly synthesis of nanoparticles is implemented to lodge several biological components (e.g., bacteria, fungi, algae, and different plant parts and extracts). The use of plant extracts has been proven to be a quite easy and simple route for large-scale nanoparticles production when compared to either bacteria or fungi-based synthesis. Green nanoparticles synthesized using biological components are collectively recognized as biogenic nanoparticles.

2 Miniaturization and Microfabrication

The current trend is heading toward using disposable and portable sensors that are pliable to miniaturization. A sensor is a tiny device which transforms chemical or biochemical data into a signal; it commonly comprises a recognition element, transducer, and signal processor, as three main parts, as shown in Fig. 1. The transducer functioned by transforming the signal obtained by the sensor into an electrical signal. Due to current progress in instrumentation and electronics very small electrical signals can now be measured to enable on/in site pollution monitoring. Different

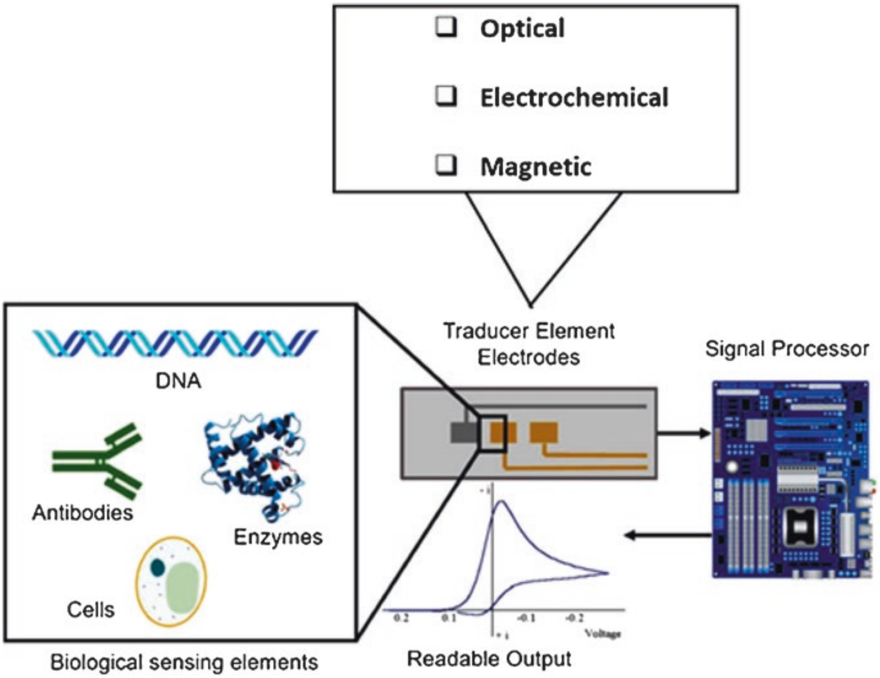


Fig. 1 Scheme of an electrochemical biosensor composition

Table 1 Types of sensors based on the transducer used for detection of chemical species

Type of sensors	Example(s)
Electrochemical	Biosensors, potentiometric sensors, and voltammetric sensors
Calorimetric	Thermistor
Optical	Spectrophotometric, colorimetric, fiber optic
Surface plasmon resonance	Biomolecule concentration

types of sensors based on transducers are mentioned in Table 1. Miniaturization along with automation, have been the emphasis of growing efforts recently. Such miniaturization, implicit by the new terminology "lab on a chip," leads to less reagent consumption, less in-flow injection analysis approaches, and the ability to use the analysis system outside the laboratory. The aim of "lab on a chip" is that the whole process is conducted by means of a microfluidic system on the same device throughout, integrating all the steps and phases of pretreatment followed by separation and finally detection. Their fabrication is usually accompanied by some special challenges in terms of accuracy, precision, reproducibility, calibration, and so on that cannot be figured out in similar ways for conventional ones. (Rios et al. 2006). Many criteria have to be fulfilled within miniaturized systems to ensure their successful implantation including being probably disposable and being robust, and they require a minimum direct operator intervention, especially for environmental applications.

Microfabrication of lab-on-chip assays use clearly less reagents compared to classical bench methodologies and improve reaction kinetics and reduce overall reaction cost (Shitanda et al. 2011 and Das et al. 2011). Recently, a massive range of electrochemical devices has been developed for detection and monitoring of various organic and inorganic toxins, for instance, heavy metals (Choi and Kim 2009, Cooper et al. 2007 and Beni et al. 2005). Similarly, the use of disposable screen-printed electrodes has added new breadth to electrochemical analysis, particularly in support of speedy and sensitive monitoring of several materials with various characteristics and properties (Renedo et al. 2007).

3 Eco-Friendly Sensor/Biosensor Development

The reliability and efficiency of an electrochemical sensor highly depend on the constitution of the detection platform. The synergistic effect between the technology of electrochemical sensors and nanomaterials has offered many merits in novel transducing context, alongside signal enhancement. Carbon paste electrodes (CPE) have been modified by linking CPE with other distinctive substances to produce chemically modified carbon electrodes showing very high selectivity. They have valuable advantages like being easy to manufacture, low cost, wider operational window, stability, and flexibility in composition to fit for different purposes (Svancara et al. 2009). Modifiers like bismuth (Bi) nanoparticles (Rico et al. 2009), hydroxyapatite (HA) (El Mhammedi et al. 2007), and Bi-HA (Khan and Abdullah 2014) have been used, with higher sensitivity, to enhance cadmium and lead deposition through HA ion-exchange. There has also been an increasing trend of using plant tissues to prepare chemically modified carbon electrodes (CMEs) with many merits including simplicity of construction, being environmentally friendly, and being less harmful. Plant tissues CME was initially fabricated and used for L-glutamate determination. Table 2 shows some plant and animal materials used as modifiers for heavy metal detection (Kwon et al. 2000).

Sensors with plant extract modifiers contain several chemical components that function as active constituents for analyte binding. Amino acids can serve as a ligand for a variety of metal ions due to the large number of donor atoms they contain. Likewise, lignin and lignocellulosic materials can be used as binding sites for metals due to the oxygen-containing functional groups, for example, alcohol,

Table 2 Examples of some modifiers of plant and animal origin

Modifier	Detection limit (ppm)
Plant origin	
Kapok fiber	1000
Apple peelings	–
Grass weed	10
Solanum tuberosum (potato)	–
Stems from cabbage	–
Banana	100
Animal origin	
Feather	121

phenol, and carboxylic acid structures in lignin that are in control for highly stable lignin–metal complexes via different bonding interactions. Likewise, cellulose, by its carbonyl and hydroxyl functional groups, can work as binding sites for different metals (Nazir et al. 2013).

4 Sensors/Biosensors Composition

Sensors technologies based on nanomaterials have been developed over the last two decades targeting the sensitive and highly specific detection and monitoring of environmental pollutants with many superior advantages of easy use, low cost, field-deployable technology. In general, sensors are composed of three main components: nanomaterials, recognition element (to increase selectivity), and a signal transduction means for analyte detection, as summarized in Fig. 1. Sensors are generally characterized on the basis of these three elements.

4.1 Nanomaterials

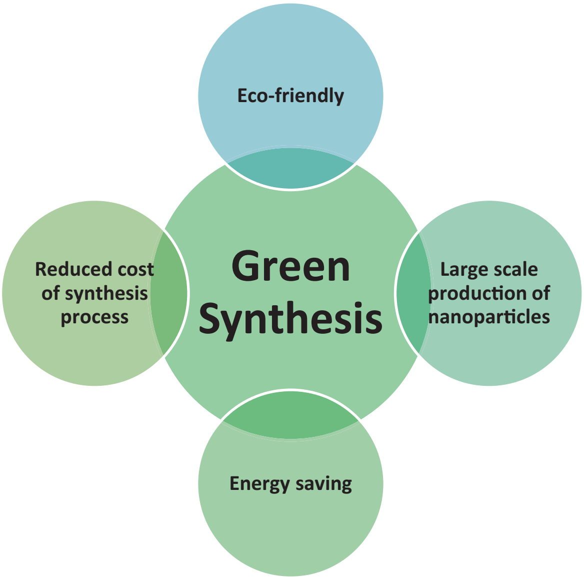
Nanomaterials have reinforced improvements and advances in sensor design in the direction of more sustainability, for instance, miniaturization, portability, disposability, and rapid signal response. Simplified surface functionalization and the high surface area-to-volume ratio support better sensors sensitivity and improve selectivity and reduce the detection limits to extreme low values. Graphene and carbon nanotubes are frequently used in nanosensors due to their large surface area, perfect electrical ad thermal conductivity, and improved mechanical strength (Yang et al. 2010). Metal and metal oxides nanoparticles have extensive uses in sensor fabrications for various applications as they can be produced in many different shapes with different extinction coefficients (Link and El-Sayed 1999) and easily modified by surface functionalization. Colloidal solutions of both silver and gold nanoparticles are widely used and due to their distinctive characteristics and color changes that make them useful as visual colorimetric sensors. Added to that, their nanoparticles excitation can cause the uniform oscillation of conduction electrons that leads to localized surface plasmon resonance–based spectroscopies, for example, surface enhanced Raman spectroscopy and surface plasmon resonance (Romo-Herrera et al. 2011). Gold nanoparticles are stable, biocompatible, and have been widely used in sensing applications (Saha et al. 2012). Surface coatings can be used for modification purposes and simplify the addition of recognition elements. Thioglycolic acid and 3-mercaptopropionic acid, thiol capping agents, are frequently used to afford chemical functionality and colloidal stability. A wide range of nanostructured metal oxides, for example, iron oxides, zinc oxides, titanium oxides, zirconium oxides, and others, have been tried for sensing uses. Quantum dots (QDs) are semiconductor nanocrystals and normally have broad absorption bands, yet narrow fluorescence emission bands; therefore they can superbly serve as optical transducers.

4.1.1 Green Synthesis of Metal/Metals Oxide Nanoparticles

An innovative era of green synthesis methodologies is attaining prodigious focus in the modern research and material improvement. Nanoparticle green synthesis is composed of single bio-reduction step methodology that necessitates fairly low consumption of energy and is also cost-effective, and allows for large-scale production of nanoparticles (Wadhwani et al. 2016), Fig. 2 illustrates the key merits of green synthesis. Ultimately, regulated and controlled green synthesis of materials/nanomaterials will directly assist elevating their environmental friendliness. Prevention/minimization of waste, using safer solvent/reagents and reduction of pollution are all considered some of the main principles for green synthesis. Solvents are an essential element in the greening of synthesis methods. Ideally, water is always the solvent of choice for green synthesis processes, for example, synthesis of Ag and Au nanoparticles using gallic acid in an aqueous medium at room temperature (Yoosaf et al. 2007). Ionic liquids are also acknowledged for being eco-friendly and can be used for synthesis of various metal nanoparticles (Vollmer et al. 2010). Ionic liquids are able to work both as a reducing and a protecting agent; this facilitates and simplifies the nanoparticle synthesis process.

Various reaction parameters like temperature, solvent, pH and pressure can affect and control green synthesis methodologies. One of the highly considered factor in metal/metal oxide nanoparticles synthesis is biodiversity in plants because of the presence of different useful phytochemicals within different plants, for instance, aldehydes, ketones, phenols, carboxylic acids, amides, ascorbic acids, flavones, and terpenoids in different percentages based on cultivation location, season and species,

Fig. 2 Significant virtues of green synthesis



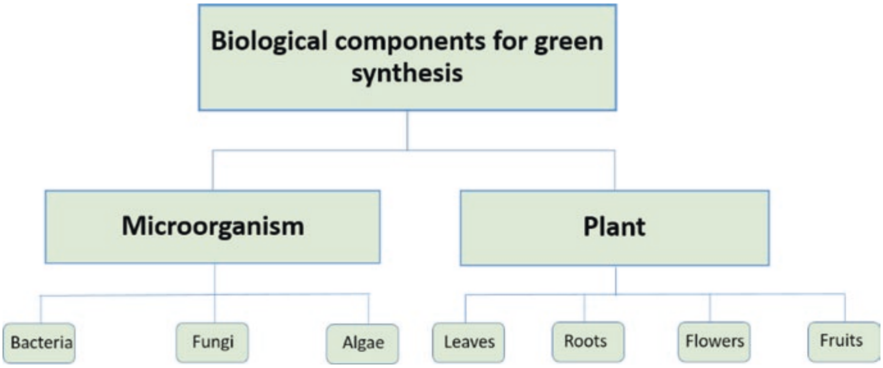


Fig. 3 Different biological components used for green synthesis

and other factors. These components reduce metal salts into metal nanoparticles. Figure 3 summarizes the currently used biological components for green synthesis.

4.1.2 Bacteria

Bacterial species, mainly prokaryotic and actinomycetes, have been broadly used for biotechnological applications (Gericke and Pinches 2006). With a relatively easy manipulation, bacteria owns the capability of reducing metal ions and considered as significant parameter in the preparation of various nanoparticles (Iravani 2014; Thakkar et al. 2010). Some strains of bacteria have expansively been

Table 3 Examples of metallic nanoparticles prepared from biological components

Organism	Species	Nanoparticles	Applications	Ref.
Bacteria	*Klebsiella pneumonia*, *E. coli*	Ag	Electrical batteries, optical receptors	Ahmad et al. (2010)
	Bacillus megaterium D01	Au	Bio sensing, catalysis	Wen et al. (2009)
	E. coli DH 5α	Ag	Hemoglobin electrochemistry	Du et al. (2007)
Fungi	*Verticillium*	Ag	Catalysis	Mukherjee et al. (2001)
	Fusarium semitectum	Ag	Bio-labeling	Basavaraja et al. (2008)
	Verticillium luteoalbum	Au	Optics, sensor, coatings	Gericke and Pinches (2006)
	Aspergillus terreus	ZnO	Bio sensing, catalysis	Raliya and Tarafdar (2014)
Yeast	MKY3	Ag	Coatings, electrical batteries	Kowshik et al. (2002)
	Saccharomyces cerevisiae broth	Ag, Au	Catalysis	Mourato et al. (2011)
Plant	*Aloe barbadensis*, Miller	Au, Ag	Optical coatings	Chandran et al. (2006)
	Azadirachta indica	Ag, Au	Toxic metals remediation	Shankar et al. (2004)
	Camellia sinensis	Ag, Au	Sensors, catalysts	Raliya and Tarafdar (2014)
	Medicago sativa	Au	Labeling in structural biology	Gardea-Torresdey et al. (2002)

investigated for the green production of silver nanoparticles, for instance, *Escherichia coli*, *Enterobacter cloacae*, *Lactobacillus casei*, *Bacillus cereus*, *Pseudomonas proteolytica*, *Bacillus indicus*, *Bacillus amyloliquefaciens*, and others. Similarly, gold nanoparticles are bio-reduced using several bacterial species, for instance, *Desulfovibrio desulfuricans*, *E. coli* DH5a, *Bacillus megaterium*, and others. Distinct size/shape and morphology can be obtained as summarized in Table 3.

4.1.3 Fungi

Biosynthesis of metal/metal oxide nanoparticles based on fungi as a biological element is a very competent development for green nanoparticles generation. Owing to the presence of intracellular enzyme in addition to enzymes, proteins, and other reducing elements on the fungi cell surfaces, make them a better biological agents for the nanoparticles preparation (Chen et al. 2009; Narayanan and Sakthivel 2011). Efficient fungi can produce greater amounts of nanoparticles rather than bacteria

(Mohanpuria et al. 2008). Reductase enzymatic reduction is the most probable mechanism for the metallic nanoparticle formation. Various fungal species can be used for the synthesis of nanoparticles of several metals and metals oxides like gold, silver, zinc oxide, and titanium dioxide, and synthesis of other components, Table 3.

4.1.4 Yeast

There are around 1500 yeast species that have been recognized. Many research groups have reported successful synthesis trials of nanoparticles/nanomaterials by the use of yeast. *Saccharomyces cerevisiae* broth and silver-tolerant yeast strain have been reported to successfully produce silver and gold nanoparticles (Yurkov et al. 2011). Various species are incorporated for numerous metallic nanoparticles preparation (Table 3).

4.1.5 Plants

Plants can store specific amounts of heavy metals. Consequently, biosynthesis practices using plant extracts have acquired amplified attention as a simple, feasible, efficient, and cost-effective methods along with being an excellent alternate to traditional methods of nanoparticles preparation, as illustrated in Fig. 4. Plants contain organic biomolecules, for instance, proteins, carbohydrates, and coenzymes, that are capable of reducing metal salts to their nanoparticles in a single step process. Many plants including neem, aloe vera, oat, tulsi, coriander, mustard, lemon grass, and lemon have been extensively used for silver and gold nanoparticle synthesis, as described in Table 3.

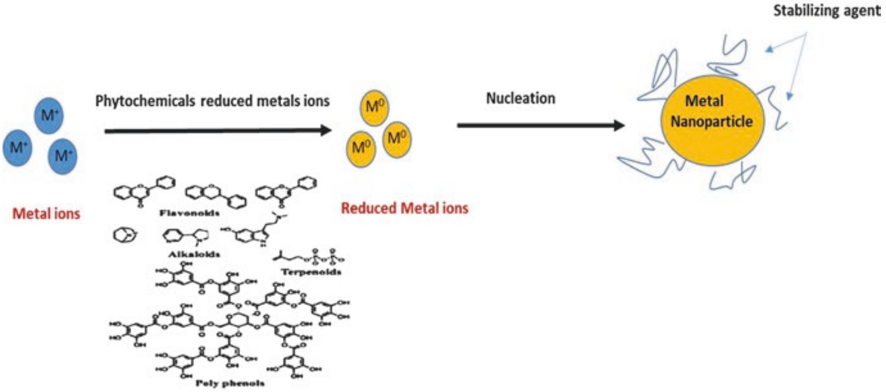


Fig. 4 Mechanism of nanoparticle formation by plant leaf extracts

4.2 Recognition Elements

Selectivity is crucial property in the design of an efficacious sensor. A wide range of recognition elements have been executed in the design of nanosensor that includes antibodies (Jiajie et al. 2014), aptamers (Ma et al. 2013) functional proteins (Bies et al. 2004), enzymes (Evtugyn et al. 1998), and whole cells (Olaniran et al. 2011).

4.2.1 Antibodies

Antibodies bind specifically to a distinct antigen, and they are commonly used for capturing and labeling microorganisms or substances that evoke an immune response (Ellington et al. 2010). Three types of antibodies used to recognize the analytes: polyclonal, monoclonal, and antibody fragments. Though antibodies are commonly utilized in biosensor fabrication, they have some drawbacks such as high costs, pH sensitivity, short shelf-lives, temperature, and batch-to batch variations (Bordeaux et al. 2010). Even with these weaknesses, antibodies are regularly the most selective recognition means for immunogenic analytes (Huang et al. 2005). Many immunosensors and screen-printed electrodes are designed and used for the detection of environmental pollutants as multi-analytes in different settings and are offered both as a laboratory device and a portable system.

4.2.2 Aptamers

Aptamers can be defined as short oligonucleotide of RNA or ssDNA that can bind to certain molecules. Aptamers have long shelf-lives, have low variability between batches, are thermally stable, and have low cost production compared to antibodies (Low et al. 2009; Hamula et al. 2011). Aptamers of nucleic acid are known for their high specificity (Hoinka et al. 2015). The oligonucleotide sequences are isolated, identified and amplified through polymerase chain reaction and affinity testing, and after de novo synthesis they can be integrated into biosensors (Tombelli et al. 2002). Bacteria and pathogenic microorganisms were detected using aptamers-based sensors with optical detection in different environment matrices, air and drinking water, and food samples too.

4.2.3 Enzymes

Enzyme-based biosensors are having increasing significance and abundance in environmental and food applications. Improvement of enzyme biosensors using different strategies were done, for example, electrochemical interfaces to enzymes (Chen and Gorski 2001), application of quinoproteins (Matsushita et al. 2002) and metalloproteins (Sinibaldi et al. 2001), and investigations on immobilization (Gill and Ballesteros 2000). Acetylcholine esterase was used to detect organophosphates and carbamates with either single-use devices (Schulze et al. 2002) or in traditional graphite electrodes. For instant detecting phenols in environmental matrices was done using continuous electrochemical sensor (Freire et al. 2002) going up to biosensor arrays (Young et al. 2001). Toxic gas can also be detected using enzyme-based sensors. For example, SO_2 was detected by screen-printed electrodes (Hart et al. 2002). Nitrite reductase-based optical biosensor was used for monitoring purposes. In addition heavy metals and nitrite can be detected in potable water using several biosensors (Lee and Lee 2002).

4.2.4 Whole Cells

Whole cell-mediated biosensors are founded on the use of biosensing cells, for instance, microorganisms, protozoa, algae, and plant cells. Being cheaper gives an advantage to whole cell-based biosensors compared to enzyme-based biosensors. Multistep reactions are usually possible since all the enzymes and cofactors needed are present in one cell. Many microbial-mediated optical biosensors have been designed and used for toxicity and pollutants detection (Olaniran et al. 2011). *A rapid and effective heavy metals monitoring in waste water was achievable by* a whole-cell bacterial biosensors (Olaniran et al. 2011). Because of the use of *Shigella sonnei* and *Escherichia coli*, the sensors were recording high sensitivity. An integrated fluorescence-based sensor was reported to monitor bacterial respiratory activity by measuring the reduction in oxygen partial pressure and pH value reduction (Arain et al. 2006).

4.3 Signal Transduction

There are three chief signal transduction means used in nanomaterials-mediated sensors, namely, optical, electrochemical, and magnetic methods.

4.3.1 Optical

Optical transduction takes place because of the interaction between electromagnetic radiation (ultraviolet, visible, or infrared light) and the sensing element. The two widely used optical methods employed in the design of nanosensor are surface plasmon resonance and fluorescence. Quantum dots or polymer nanoparticle probes or dye-doped silicon is commonly used in fluorescent nanosensors due to their photostability and robustness (Vikesland and Wigginton 2010).

4.3.2 Electrochemical

Electrochemical methods of detection works by measuring the change in potential or current resulting from the reaction between the analyte and the electrode. Different methods can be used for change detection including amperometry, cyclic voltammetry, chronopotentiometry, chronoamperometry, and impedance spectroscopy (Grieshaber et al. 2008).

4.3.3 Magnetic

Magnetic transduction has been incorporated to detect signals upon analyzing biological samples due to the low background magnetic signal (Koets et al. 2009).

5 Environmental Applications for Sensors/Biosensors

There are vast of environment contaminants that can be accurately detected and monitored via sensors/biosensors using antibodies, enzymes, and aptamers as recognition elements. Different environmental applications are summarized in Fig. 5.

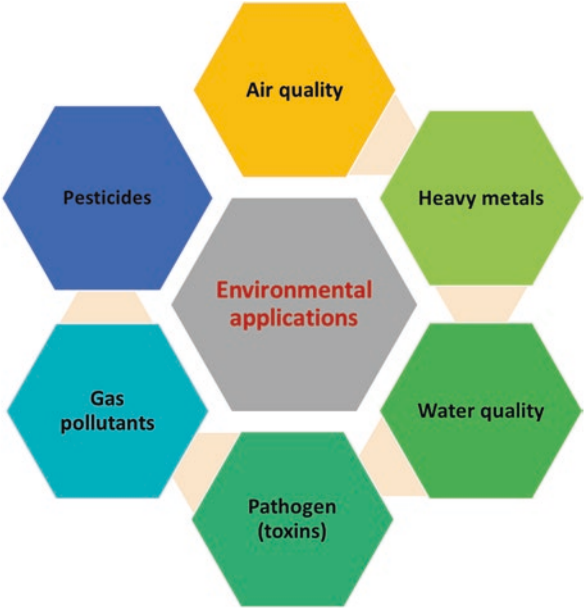


Fig. 5 Environmental applications of sensors/biosensors

5.1 Pesticides

Owing to their significant environmental existence, pesticides are among the utmost crucial environmental pollutants. Currently, over 800 active ingredients are present in pesticides (Liu et al. 2013). Organophosphates (OP), carbamates, neonicotinoids, and triazines are the prevailing ones. The organophosphates insecticides are broadly used in agriculture but they have the topmost environmental concern because of their unlimited harmfulness. Consequently, simple, sensitive, reliable, and sustainable approaches such as biosensors have been used to detect and monitor the pesticides with minimum sample pretreatment procedures. Table 4 describes a summary of some latest biosensors for pesticides detection and monitoring.

5.1.1 Organophosphates

Paraoxon has been detected by the aid of disposable amperometric acetylcholinesterase-based biosensors on gold screen-printed electrodes in water samples (Arduini et al. 2013). The disposable biosensors showed a good analytical performance in regard to linearity, sensitivity, and detection limits due to the proper enzyme immobilization by the self-assembled monolayer. Other biosensors for paroxon detection were fabricated (Arduini et al. 2015) using butyrylcholinesterase and carbon black nanoparticles that added some advantages such as low applied potential, cost-effectiveness, and ease of preparing a stable dispersion (Arduini et al. 2015). Gold nanorods were also used in colorimetric acetylcholinesterase biosensor (Guo et al. 2017) to detect paraoxon in real water samples. Besides, the colorimetric biosensor allowed paraoxon detection in irrigation water with good recoveries.

Methyl parathion, was determined by hydrolase- based biosensor using magnetic Fe_3O_4 nanocomposite and gold nanoparticles with high sensitivity and selectivity (Zhao et al. 2013). The advantages of using hydrolase were; no poisoning by organophosphates, produces a reusable biosensor and allows the continuous measurement (Zhao et al. 2013). Due to great catalytic effectiveness, high conductivity, and being exceptionally biocompatible, biosensors using gold nanoparticles showed wide linear range and high sensitivity. Another acetylcholinesterase amperometric biosensor was used for methyl parathion detection in contaminated lake, for immobilization purpose a graphite working electrode and macroalgae were employed (Nunes et al. 2014). Another acetylcholinesterase-based biosensor for methyl parathion detection was fabricated using a nanoporous carbon paste electrode with gold nanoparticles, chitosan, and Nafion (Deng et al. 2016). Determination of chlorpyrifos in river water samples was done at low cost by disposable tyrosinase based biosensor on screen printed electrodes (Mayorga-Martinez et al. 2014) and aptasensor using a new composite film (Wei et al. 2014). Dichlorvos detection in environmental samples was achieved using several biosensors that constructed via bi-enzyme system composed of acetylcholinesterase in addition to choline oxidase

Table 4 Biosensors for pesticide monitoring

Pesticide	Biosensor type	Sensing material	Recognition element	Ref.
Paraoxon	Electrochemical	Gold SPE^a + cysteamine SAM^b	Acetylcholinesterase enzyme	Arduini et al. (2013)
	Electrochemical	SPE^a + carbon black NP^c	Butyrylcholinesterase enzyme	Arduini et al. (2015)
	Optical	Iodine-starch	Acetylcholinesterase and choline oxidase enzymes	Gao et al. (2012)
Methyl parathion	Electrochemical	SPE^a with Fe_3O_4 + gold NP^c	Hydrolase enzyme	Zhao et al. (2013)
	Electrochemical	Graphite + macroalgae	Acetylcholinesterase enzyme	Nunes et al. (2014)
	Electrochemical	$NiCo_2S_4$ reticulated spheres in carbon electrode	Acetylcholinesterase enzyme	Deng et al. (2016)
Acetamiprid	Electrochemical	Gold NP^c + MWCNT^d + rGO^e nanoribbons	Aptamers	Fei et al. (2015)
	Electrochemical	Silver NP^c + nitrogen doped GO^f	Aptamers	Jiang et al. (2015)
	Optical	Gold NP^c	Aptamers	Shi et al. (2013)
Dichlorvos	Optical	QD^g + acetylcholine	Enzyme (AChE^c + ChO^e)	Meng et al. (2013)
	Electrochemical	Platinum electrode + ZnO	Acetylcholinesterase enzyme	Sundarmurugasan et al. (2016)
	Electrochemical	Ionic liquids-gold NP^c + porous carbon comp	Acetylcholinesterase enzyme	Wei et al. (2014)
Chlorpyrifos	Electrochemical	SPCE^h and IrOx NP^c	Enzyme (tyrosinase)	Mayorga-Martinez et al. (2014)
	Electrochemical	Boron-doped diamond electrode + gold NP^c	Acetylcholinesterase enzyme	Wei et al. (2014) Chai et al. (2013) Oliveira et al. (2013)
Pirimicarb	Electrochemical	Prussian blue + MWCNT^d SPE^a	Acetylcholinesterase enzyme	
	Electrochemical	Carbon paste electrode + MWCNT^d	Laccase enzyme	
Atrazine	Electrochemical	Gold NP^c	Monoclonal antibodies	Liu et al. (2014a, b)
	Electrochemical	SWCNT^i	Monoclonal antibodies	Belkhamssa et al. (2016a, b)
	Electrochemical	Magnetic beads + G protein	Phage–antibody complex	González-Techera et al. (2015)

Carbofuran	Electrochemical	IrOx-chitosan nanocomposite	Acetylcholinesterase enzyme	Jeyapragasam and Saraswathi (2014)
	Electrochemical	GCE[j] with GO[f] + MWCNT[d]	Acetylcholinesterase enzyme	Li et al. (2017)
	Electrochemical	GCE[j] + NiO NP[c] + COOH graphene-Nafion	Acetylcholinesterase enzyme	Yang et al. (2013)
Fenitrothion	Electrochemical	Carbon paste electrode	Whole cell (Pseudomonas putida JS444)	Lei et al. (2007)

[a] *SPE* screen printed electrode

[b] *SAM* self-assembled monolayer

[c] NP nanoparticles

[d] *MWCNT* multiwalled carbon nanotubes

[e] *rGO* reduced graphene oxide

[f] *GO* graphene oxide

[g] *QD* quantum dots

[h] *SPCE* screen-printed carbon electrode

[i] *SWCNT* single-walled carbon nanotubes

[j] *GCE* glassy carbon electrode

(Meng et al. 2013), a platinum electrode modified with acetylcholinesterase-zinc oxide (Sundarmurugasan et al. 2016) and a composite of ionic liquids, gold nanoparticles, and porous carbon (Peng et al. 2017). The combination of ionic liquid, porous carbon, and gold nanoparticles improves the adsorption of enzyme, preserves the activity of enzyme, and enhances the sensitivity of the analysis, Table 4.

5.1.2 Other Types of Pesticides

Acetamiprid analysis in water samples has been achieved by impedimetric aptasensors (Fei et al. 2015). Gold nanoparticles, a composite composed of reduced graphene oxide nanoribbons along with multiwalled carbon nanotubes were utilized, which cause higher electron transfer with overall improvement of analytical performance (Fei et al. 2015). Atrazine was analyzed in crop samples using an electrochemical immunosensor based on gold nanoparticles (Liu et al. 2014a, b) and in seawater/river water samples using a disposable immunosensor with single-walled carbon nanotubes (Belkhamssa et al. 2016a, b). A novel recognition element formed by recombinant complex of antibody/ M13 phage and G protein functionalized magnetic beads was used in fabrication of atrazine electrochemical immunosensor (González-Techera et al. 2015).The biosensor displayed a boosted detection limit due to high sensitivity of phage/antibody complex (González-Techera et al. 2015).

Enzymatic biosensors were used to determine pirimicarb using enzymatic laccase and multiwalled carbon nanotubes on carbon paste electrode composite (Chai et al. 2013). Carbofuran, a carbamate insecticide, was determined by acetylcholinesterase biosensor immobilized onto iron oxide–chitosan nanocomposite with square wave voltammetry (Jeyapragasam and Saraswathi 2014). A superior limit of detection was achieved by immobilizing acetylcholinesterase using modified electrode with (nickel oxide +Nafion+ carboxylic graphene) to detect carbofuran in a mixture with methyl parathion and chlorpyrifos (Yang et al. 2013). It was suggested that the conjugation of nickel oxide nanoparticles and carboxylic graphene decrease oxidation peak potential and increase the electron transfer (Yang et al. 2013), Table 4.

5.2 Metals

Nano-enabled sensors have been effectively utilized to detect and monitor a number of heavy metals in different environmental matrices. From these metals are mercury, lead, chromium, and cadmium.

5.2.1 Mercury

There is usually an extensive research concern for Mercury detection due to its known negative neurological effects to humans (Selid et al. 2009). Production of DNA-based probes is a main emphasis of mercury nanosensor development (Liu

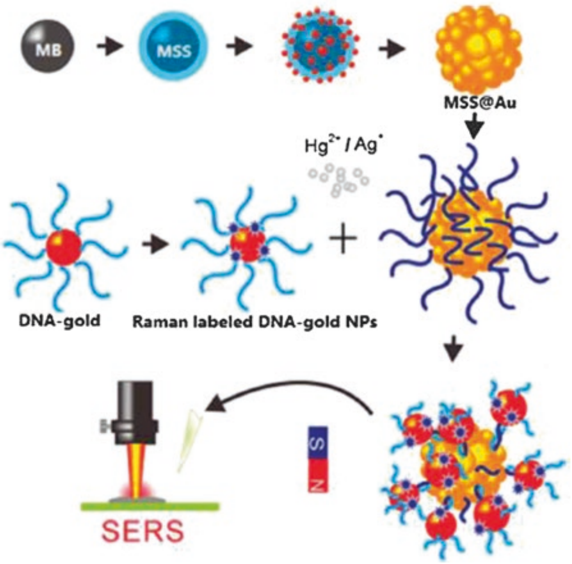


Fig. 6 Schematic of surface enhanced Raman spectroscopy (SERS)-active system for Hg*II* ion detection based on T–Hg–T bridges using DNA-Au NPs and DNA-MSS@Au NPs (Reprinted with permission from Liu et al. 2014a, b Copyright 2014 American Chemical Society)

et al. 2014a, b). In DNA, the base mismatch of thymine–thymine are of significant finding in case of mercury presence due to metal base pairs formation. Many mercury sensors have been fabricated with several nanomaterials, for example using mercury sandwich type assay (Liu et al. 2014a, b) where spheres of magnetic silica are captured into gold shell along with gold nanoparticles attached to complementary sequences of DNA containing five positions of mismatched thymine with an insufficient binding energy not to allow complete hybridization, as shown in Fig. 6. In the presence of mercury, full hybridization took place, hence reducing the inter-probe spacing and generating a plasmonic hotspot. Thiol based assays for the detection of mercury have been severally using various nanoparticles, for instance, gold (Chansuvarn et al. 2015), silver (Alam et al. 2015) or quantum dots (Ke et al. 2012). Likewise, a competition-based reaction assay wherein surface coating is replaced with mercury has been designated (Huang and Chang 2006). It was reported that thiol coatings improved the assay specificity.

5.2.2 Lead

Lead can result in higher risk of different types of cancer and neurological problems (Goyer 1990) consequently, lead detection is considered as a chief concern. Various nanosensors have been constructed for lead analysis. 8–17 DNAzyme and catalytic nucleic acid were used for label-based lead detection (Tang et al. 2013), in addition to a class of oligonucleotides capable of formation of G-quadruplexes in lead presence (Li et al. 2010). An AlOOH–graphene oxide nanocomposite for detection of lead and other metals like cadmium by voltammetry was investigated (Gao et al. 2012), the great adsorption capacity of AlOOH to form a composite results in the electron transfer kinetics. The AlOOH does not show good selectivity for a single metal; thus, the AlOOH–graphene oxide nanocomposite is considered a good option for multiplex detection.

5.2.3 Chromium

High chromium absorption can result in several health problems, for example, airway hypersensitivity, nasal and lung cancer, and other types of tumors and fibroproliferative diseases, (Gibb et al. 2000). Several immunoassays have been suggested for chromium detection (Liu et al. 2012). A new anti-CrIII-EDTA antibody was developed for chromium detection via immunochromatographic assay. In order to ensure evoking an immune response, chromium ions were mixed with bifunctional chelating agent, isothiocyanobenzyl-EDTA then linked to a carrier protein to reach an appropriate size for ultimate, sensitive, and rapid detection (Liu et al. 2012).

5.2.4 Cadmium

A diversity of nanomaterials have been investigated for cadmium detection, this includes quantum dots (Gui et al. 2012, 2013), SWCNT (Sun et al. 2007), and antimony nanoparticles (Toghill et al. 2009). An off/on- fluorescence sensor for cadmium detection was designed (Gui et al. 2012,). First, Photoluminescent CdTe/CdS quantum dots were quenched using ammonium pyrrolidine dithiocarbamate, upon introducing cadmium ions, it displaced the quenching agent from the QD surface and reinstated the photoluminescence; therefore, turning on the sensor. These sensors showed high selectivity for cadmium, and to improve their accuracy, a ratiometric sensor was later developed (Luan et al. 2012).

5.3 Toxins

Many sensors were constructed for detection and monitoring of various toxins (Eissa et al. 2015). Brvetoxin was detected with a sensitive and selective aptasensor by gold electrodes modified via cysteamine SAM (Eissa et al. 2015). A further detection of brevetoxin and saxitoxin was reported using cardiomyocyte-based portable biosensor (Wang et al. 2015). Cardiomyocytes provided real-time screening of pathogens in a rapid manner detection. Microcystin-LR detection in water samples was performed using graphene electrochemical impedance spectroscopy immunosensor and showed good reproducibility and repeatability results (Zhang et al. 2017a, b). A better detection limit for microcystin-LR detection in the studies samples of lake water was achieved using immunosensor with gold electrodes modified with a molybdenum disulfide–gold nanorod composite (Zhang et al. 2017a, b). This improvement could be explained by the augmented effect of gold nanorods and

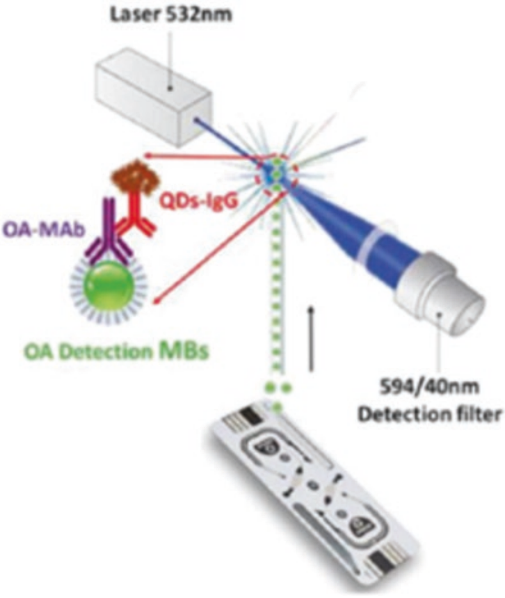


Fig. 7 Working principle of fluorescence immunosensor for detection of okadaic acid reprinted from Pan et al. (2017)

molybdenum disulfide that endorsed larger surface area, increasing electrical conductivity and overall electrochemical performance.

Okadaic acid toxin in algal, shellfish and seawater can be detected using different biosensors (McNamee et al. 2013, Pan et al. 2017). For okadaic acid, saxitoxin, and domoic acid determination in seawater and algal samples, fabrication of multiplex surface plasmon resonance biosensor was reported (McNamee et al. 2013). A multiplex immunological method was developed to be used as an early warning tool for variable marine biotoxin monitoring in seawater samples. A highly sensitive fluorescence-based immunosensor using CdTe QDs and carboxylic acid modified magnetic beads was investigated for the analysis of okadaic acid in mussel (Pan et al. 2017). An illustration of the fluorescence immunosensor working principle is shown in Fig. 7.

To detect domoic acid toxin, carbon nanotube disposable immunosensors were fabricated and showed good reproducibility and low limit of detection when analyzing the seawater samples (Marques et al. 2017). For improving the detection limit an underwater surface plasmon resonance biosensor was designed (Colas et al. 2016); in addition, it also allows for in situ quantitative determination of domoic acid in seawater.

5.4 Endocrine Disrupting Chemicals

Detection of bisphenol A, an endocrine disrupting chemical, in water samples was achieved by using fluorescence aptasensors (functionalized by fluorescein amidite) and gold nanoparticles (Ragavan et al. 2013). A portable, fast, and cost-effective evanescent-wave optical fiber aptasensor was successfully used for sensitive detection of bisphenol A in water samples with no need of pretreatment procedures (Yildirim et al. 2014).

17β-estradiol was monitored in lake water using CdSe nanoparticles and TiO_2 nanotube arrays aptasensor with an outstanding selectivity and femtomolar level of detection. The particular recognition reaction takes place between the 17-estradiol and aptamer and leads to an increase in the steric hindrances to the electron donor diffusion, which leads to a decrease of the photocurrent, thereby resulting in in situ complex formation. The superior selectivity toward 17-estradiol could be credited to the excellent photoelectrical activity, the tubular microstructure of sensing interface, high affinity of the aptamer to 17β-estradiol, and large packing density of aptamer (Fan et al. 2014).

6 Challenges and Future Perspectives

It is obvious that the future trends and the forthcoming advances of sensors/biosensors will count on the achievements of evolving micro- and nano-level technologies including electronics, materials science, physics, and biochemistry. Since environmental pollution within various media is growing incredibly fast and becoming a severe global fear, designing and developing novel biosensor-based techniques capable of precisely identifying and analyzing different pollutants from a larger spectrum is of high significance. Nevertheless, sensors/biosensors for environmental monitoring have some limitations including response time, selectivity, sensitivity, stability, and lifetime. Researchers have to collaborate in work to eliminate these limitations for effective eco-friendly, reliable, competitive tools of analysis.

It is also clear that need for speedy detecting tools like biosensors will grow in the upcoming future. Despite the current and past significant research and efforts in electrochemical sensor development field, a challenge to improve devices to evade instrumental errors and improve reliability in complex matrices is still crucial. Sensors have to fulfil all demands for proper, robust, and sustainable monitoring by being integrated networks, offering screening and analysis of complex mixtures of multi-analytes and providing remote sensing through combining with wireless signal transmitters. In this context, comprehensive studies and research are required in the fields of biosensors, bioelectronics, and bionanotechnology that will definitely have a manifest impact on expanding innovative biosensing approaches, putting into consideration being "smart" and user friendly to fit more into the future.

7 Conclusion

Researchers' effort is being focused in the direction of designing and developing reliable, sustainable, and more sensitive methods of analysis that are able to detect, monitor, and eliminate noxious environmental contaminants. Being able to give more sensitive, selective, robust, and low-cost results in addition of being eco-friendly, sensors are rapidly becoming a vital deliberation in all environmental screening and monitoring programs. Shifts from classical harmful mercury-based electrodes with low sensitivity and stability and lifetime problems to disposable electrodes with inert green materials, improved stability are among the essential routes explored. Consequently, selection of appropriate sensing and modifying materials, miniaturization and green synthesis approaches are of supreme importance toward sustainability of environmental analysis. Together with methods optimization, reliable analyses should guard public health and improve the quality of the environment.

References

Ahmad N, Sharma S, Alam MK et al (2010) Rapid synthesis of silver nanoparticles using dried medicinal plant of basil. Colloids Surf B Biointerfaces 81:81–86. https://doi.org/10.1016/j.colsurfb.2010.06.029

Alam A, Ravindran A, Chandran P, Sudheer Khan S (2015) Highly selective colorimetric detection and estimation of Hg^{2+} at nano-molar concentration by silver nanoparticles in the presence of glutathione. Spectrochim Acta A Mol Biomol Spectrosc 137:503–508

Arain S, John GT, Kranse C, Gerlach J, Wolfbeis OS, Klimant I (2006) Characterization of microtiterplates with integrated optical sensors for oxygen and pH, and their applications to enzyme activity screening, respirometry, and toxicological assays. Sensors Actuators B 113:639–648

Arduini F, Guidone S, Amine A, Palleschi G, Moscone D (2013) Acetylcholinesterase biosensor based on self-assembled monolayer-modified gold-screen printed electrodes for organophosphorus insecticide detection. Sensors Actuators B Chem 179:201–208

Arduini F, Forchielli M, Amine A, Neagu D, Cacciotti I, Nanni F, Moscone D, Palleschi G (2015) Screen-printed biosensor modified with carbon black nanoparticles for the determination of paraoxon based on the inhibition of butyrylcholinesterase. Microchim Acta 182:643–651

Azmuddin AM, Khan AA, Ajab H (2017) Environmental monitoring by eco-friendly fabricated carbon-modified electrode sensor. Int J Biosens Bioelectron 2(5):141–144

Basavaraja S, Balaji SD, Lagashetty A et al (2008) Extracellular biosynthesis of silver nanoparticles using the fungus Fusarium semitectum. Mater Res Bull 43:1164–1170. https://doi.org/10.1016/j.materresbull.2007.06.020

Belkhamssa N, da Costa JP, Justino CIL et al (2016a) Development of an electrochemical biosensor for alkylphenol detection. Talanta 158:30–34

Belkhamssa N, Justino CIL, Santos PSM, Cardoso S et al (2016b) Label-free disposable immunosensor for detection of atrazine. Talanta 146:430–434

Beni V, Ogurtsov V, Bakunin N et al (2005) Development of a portable electroanalytical system for the stripping voltammetry of metals: determination of copper in acetic acid soil extracts. Anal Chim Acta 552:190–200

Bies C, Lehr CM, Woodley JF (2004) Lectin-mediated drug targeting: history and applications. Adv Drug Deliv Rev 56:425–435

Bordeaux J, Welsh AW, Agarwal S, Killiam E, Baquero MT, Hanna JA, Anagnostou VK, Rimm DL (2010) Antibody validation. BioTechniques 48:197–209

Chai Y, Niu X, Chen C, Zhao H, Lan M (2013) Carbamate insecticide sensing based on acetylcholinesterase/Prussian blue-multi-walled carbon nanotubes/screen-printed electrodes. Anal Lett 46:803–817

Chandran SP, Chaudhary M, Pasricha R et al (2006) Synthesis of gold nanotriangles and silver nanoparticles using aloe vera plant extract. Biotechnol Prog. https://doi.org/10.1021/bp0501423

Chansuvarn W, Tuntulani T, Imyim A (2015) Colorimetric detection of mercury(II) based on gold nanoparticles, fluorescent gold nanoclusters and other gold-based nanomaterials. TrAC Trends Anal Chem 65:83–96

Chen L, Gorski W (2001) Bioinorganic composites for enzyme electrodes. Anal Chem 73(13):2862–2868

Chen Y-L, Tuan H-Y, Tien C-W et al (2009) Augmented biosynthesis of cadmium sulfide nanoparticles by genetically engineered *Escherichia coli*. Biotechnol Prog 25:1260–1266. https://doi.org/10.1002/btpr.199

Choi HS, Kim HD (2009) Development of a portable heavy metal ion analyzer using disposable screen-printed electrodes. Bull Kor Chem Soc 30(8):1881–1883

Colas F, Crassous M-P, Laurent S et al (2016) A surface plasmon resonance system for the underwater detection of domoic acid. Limnol Oceanogr Methods 14:456–465

Cooper J, Bolbot J, Saini S et al (2007) Electrochemical method for the rapid on site screening of cadmium and lead in soil and water samples. Water Air Soil Pollut 79(1):183–195

Das RN, Lin HT, Lauffer JM et al (2011) Printable electronics: towards materials development and device fabrication. Circuit World 37:38–45

Deng Y, Liu K, Liu Y, Dong H, Li S (2016) An novel acetylcholinesterase biosensor based on nano-porous pseudo carbon paste electrode modified with gold nanoparticles for detection of methyl parathion. J Nanosci Nanotechnol 16:9460–9467

Du L, Jiang H, Liu X, Wang E (2007) Biosynthesis of gold nanoparticles assisted by *Escherichia coli* DH5α and its application on direct electrochemistry of hemoglobin. Electrochem Commun 9:1165–1170. https://doi.org/10.1016/j.elecom.2007.01.007

Eissa S, Siaj M, Zourob M (2015) Aptamer-based competitive electrochemical biosensor for brevetoxin-2. Biosens Bioelectron 69:148–154

El Mhammedi MA, Bakasse M, Chtaini A (2007) Electrochemical studies and square wave voltammetry of paraquat at natural phosphate modified carbon paste electrode. J Hazard Mater 145(1–2):1–7

Ellington AA, Kullo IJ, Bailey KR, Klee GG (2010) Antibody-based protein multiplex platforms: technical and operational challenges. Clin Chem 56:186–193

Evtugyn GA, Budnikov HC, Nikolskaya EB (1998) Sensitivity and selectivity of electrochemical enzyme sensors for inhibitor determination. Talanta 46:465–484

Fan L, Zhao G, Shi H et al (2014) A femtomolar level and highly selective 17-estradiol photoelectrochemical aptasensor applied in environmental water samples analysis. Environ Sci Technol 48:5754–5761

Fei A, Liu Q, Huan J, Qian J, Dong X et al (2015) Label-free impedimetric aptasensor for detection of femtomole level acetamiprid using gold nanoparticles decorated multiwalled carbon nanotube-reduced graphene oxide nanoribbon composites. Biosens Bioelectron 70:122–129

Freire R, Duran N, Kubota L (2002) Electrochemical biosensor-based devices for continuous phenols monitoring in environmental matrices. J Braz Chem Soc 13(4):456–462

Gao C, Yu XY, Xu RX, Liu JH, Huang XJ (2012) AlOOH-reduced graphene oxide nanocomposites: one-pot hydrothermal synthesis and their enhanced electrochemical activity for heavy metal ions. ACS Appl Mater Interfaces 4:4672–4682

Gardea-Torresdey JL, Parsons JG, Gomez E et al (2002) Formation and growth of Au nanoparticles inside live alfalfa plants. Nano Lett 2:397–401. https://doi.org/10.1021/nl015673

Gericke M, Pinches A (2006) Microbial production of gold nanoparticles. Gold Bull 9:22–28. https://doi.org/10.1007/BF03215529

Gibb HJ, Lees PS, Pinsky PF, Rooney BC (2000) Lung cancer among workers in chromium chemical production. Am J Ind Med 38:115–126

Gill I, Ballesteros A (2000) Bioencapsulation within synthetic polymers (Part 2): non-sol-gel protein-polymer biocomposites. Trends Biotechnol 18(11):469–479

González-Techera A, Zon MA, Molina PG et al (2015) Development of a highly sensitive noncompetitive electrochemical immunosensor for the detection of atrazine by phage anti-immunocomplex assay. Biosens Bioelectron 64:650–656

Goyer RA (1990) Lead toxicity: from overt to subclinical to subtle health effects. Environ Health Perspect 86:177–181

Grieshaber D, MacKenzie R, Vörös J, Reimhult E (2008) Electrochemical biosensors—sensor principles and architectures. Sensors 8:1400–1458

Gui R, An X, Su H, Shen W, Chen Z, Wang X (2012) A near-infrared-emitting CdTe/CdS core/shell quantum dots-based OFF–ON fluorescence sensor for highly selective and sensitive detection of Cd^{2+}. Talanta 94:257–262

Gui R, An X, Huang W (2013) An improved method for ratiometric fluorescence detection of pH and Cd^{2+} using fluorescein isothiocyanatequantum dots conjugates. Anal Chim Acta 767:134–140

Guo L, Li Z, Chen H, Wu Y, Chen L, Song Z, Lin T (2017) Colorimetric biosensor for the assay of paraoxon in environmental water samples based on the iodine-starch color reaction. Anal Chim Acta 967:59–63

Hamula CLA, Zhang H, Li F, Wang Z, Le Chris X, Li X-F (2011) Selection and analytical applications of aptamers binding microbial pathogens. TrAC Trends Anal Chem 30:1587–1597

Hart J, Abass A, Cowell D (2002) Development of disposable amperometric sulfur dioxide biosensors based on screen printed electrodes. Biosens Bioelectron 17(5):389–394

Hoinka J, Berezhnoy A, Dao P, Sauna ZE, Gilboa E, Przytycka TM (2015) Large scale analysis of the mutational landscape in HT-SELEX improves aptamer discovery. Nucleic Acids Res 43:5699–5707

Huang CC, Chang H (2006) Selective gold-nanoparticle-based "turn-on" fluorescent sensors for detection of mercury (II) in aqueous solution. Anal Chem 78:8332–8338

Huang CC, Huang YF, Cao Z, Tan W, Chang HT (2005) Aptamer-modified gold nanoparticles for colorimetric determination of platelet-derived growth factors and their receptors. Anal Chem 77:5735–5741

Iravani S (2014, 2014) Bacteria in nanoparticle synthesis: current status and future prospects. Int Sch Res Not:1–18. https://doi.org/10.1155/2014/359316

Jeyapragasam T, Saraswathi R (2014) Electrochemical biosensing of carbofuran based on acetylcholinesterase immobilized onto iron oxide-chitosan nanocomposite. Sensors Actuators B Chem 191:681–687

Jiajie L, Hongwu L, Caifeng L, Qiangqiang F, Caihong H, Zhi L, Tianjiu J, Yong T (2014) Silver nanoparticle enhanced Raman scattering-based lateral flow immunoassays for ultra-sensitive detection of the heavy metal chromium. Nanotechnology 25:495501

Jiang D, Du X, Liu Q et al (2015) Silver nanoparticles anchored on nitrogen-doped graphene as a novel electrochemical biosensing platform with enhanced sensitivity for aptamer-based pesticide assay. Analyst 140:6404–6411

Ke J, Li X, Shi Y, Zhao Q, Jiang X (2012) A facile and highly sensitive probe for Hg(II) based on metal-induced aggregation of ZnSe/ZnS quantum dots. Nanoscale 4:4996–5001

Khan AAA, Abdullah MA (2014) Bismuth-modified hydroxyapatite carbon electrode for simultaneous *in-situ* cadmium and lead analysis. Int J Electrochem Sci 8:195–203

Kimmel DW, LeBlanc G, Meschievitz ME, Cliffel DE (2011) Electrochemical sensors and biosensors. Anal Chem 84:685–707

Koets M, van der Wijk T, van Eemeren JTWM, van Amerongen A, Prins MWJ (2009) Rapid DNA multi-analyte immunoassay on a magneto-resistance biosensor. Biosens Bioelectron 24:1893–1898

Kowshik M, Vogel W, Urban J et al (2002) Microbial synthesis of semiconductor PbS nanocrystallites. Adv Mater 14:815–818. https://doi.org/10.1002/1521-4095(20020605)14:11%3c815:AID-ADMA815%3e3.0.CO;2-K

Kwon HSP, Kil Yoont J, Seo ML (2000) Plant tissue-based amperometric sensor for determination of phenols in methylene chloride. J Korean Chem Soc 44(4):376–379

Lee S-M, Lee W-Y (2002) Determination of heavy metal ions using conductometric biosensor based on sol-gel-immobilized urease. Bull Kor Chem Soc 23(8):1169–1172

Lei Y, Mulchandani P et al (2007) Biosensor for direct determination of fenitrothion and EPN using recombinant Pseudomonas putida JS444 with surface-expressed organophosphorous hydrolase. 2. Modified carbon paste electrode. Appl Biochem Biotechnol 136:243–245

Li T, Wang E, Dong S (2010) Lead(II)-induced allosteric G-quadruplex DNAzyme as a colorimetric and chemiluminescence sensor for highly sensitive and selective Pb^{2+} detection. Anal Chem 82:1515–1520

Li Z, Qu S, Cui L, Zhang S (2017) Detection of carbofuran pesticide in seawater by using an enzyme biosensor. J Coast Res 80:1–5

Link S, El-Sayed MA (1999) Spectral properties and relaxation dynamics of surface plasmon electronic oscillations in gold and silver nanodots and nanorods. J Phys Chem B 103:8410–8426

Liu X, Xiang JJ, Tang Y, Zhang XL, Fu QQ, Zou JH, Lin Y (2012) Colloidal gold nanoparticle probe-based immunochromatographic assay for the rapid detection of chromium ions in water and serum samples. Anal Chim Acta 745:99–105

Liu S, Zheng Z, Li X (2013) Advances in pesticide biosensors: current status, challenges, and future perspectives. Anal Bioanal Chem 405:63–90

Liu X, Li W-J, Yang Y, Mao L-G, Peng ZA (2014a) Label-free electrochemical immunosensor based on gold nanoparticles for direct detection of atrazine. Sensors Actuators B Chem 191:408–414

Liu M, Wang Z, Zong S, Chen H, Zhu D, Wu L, Hu G, Cui Y (2014b) SERS detection and removal of mercury(II)/silver(I) using oligonucleotide-functionalized core/shell magnetic silica Sphere@Au nanoparticles. ACS Appl Mater Interfaces 6:7371–7379

Low SY, Hill JE, Peccia J (2009) DNA aptamers bind specifically and selectively to (1→3)-β-d-glucans. Biochem Biophys Res Commun 378:701–705

Luan W, Yang H, Wan Z, Yuan B, Yu X, Tu S-T (2012) Mercaptopropionic acid capped CdSe/ZnS quantum dots as fluorescence probe for lead(II). J Nanopart Res 14:1–8

Ma J, Chen Y, Hou Z, Jiang W, Wang L (2013) Selective and sensitive mercuric(II) ion detection based on quantum dots and nicking endonuclease assisted signal amplification. Biosens Bioelectron 43:84–87

Marques I, da Costa JP, Justino C, Santos P, Duarte K et al (2017) Carbon nanotube field effect biosensor for the detection of toxins in seawater. J Environ Anal Chem 97:597–605

Matsushita K, Toyama H, Yamada M, Adachi O (2002) Quinoproteins: structure, function, and biotechnological applications. Appl Microbiol Biotechnol 58(1):13–22

Mayorga-Martinez C, Pino F, Kurbanoglua S, Rivas L, Ozkan SA, Merkoci A (2014) Iridium oxide nanoparticles induced dual catalytic/inhibition based detection of phenol and pesticide compounds. J Mater Chem B 2:2233–2239

McNamee SE, Elliott CT, Delahaut P, Campbell K (2013) Multiplex biotoxin surface plasmon resonance method for marine biotoxins in algal and seawater samples. Environ Sci Pollut Res 20:6794–6807

Meng X, Wei J, Ren X, Ren J, Tang F (2013) A simple and sensitive fluorescence biosensor for detection of organophosphorus pesticides using H_2O_2-sensitive quantum dots/bi-enzyme. Biosens Bioelectron 47:402–407

Mohanpuria P, Rana NK, Yadav SK (2008) Biosynthesis of nanoparticles: technological concepts and future applications. J Nanopart Res 10:507–517

Mourato A, Gadanho M, Lino AR, Tenreiro R (2011) Biosynthesis of crystalline silver and gold nanoparticles by extremophilic yeasts. Bioinorg Chem Appl 1:1. https://doi.org/10.1155/2011/546074

Mukherjee P, Ahmad A, Mandal D et al (2001) Fungus-mediated synthesis of silver nanoparticles and their immobilization in the mycelial matrix: a novel biological approach to nanoparticle synthesis. Nano Lett 1:515–519. https://doi.org/10.1021/nl0155274

Narayanan KB, Sakthivel N (2011) Synthesis and characterization of nanogold composite using Cylindrocladium floridanum and its heterogeneous catalysis in the degradation of 4-nitrophenol. J Hazard Mater 189:519–525. https://doi.org/10.1016/j.jhazmat.2011.02.069

Nazir MS, Wahjoedi BA, Yussof AW, Abdullah MA (2013) Eco-friendly extraction, characterization and modification of microcrystalline cellulose from oil palm empty fruit bunches. BioRes 8(2):2161–2172

Nunes GS, Lins JAP, Silva FGS, Araujo LC et al (2014) Design of a macroalgae amperometric biosensor; application to the rapid monitoring of organophosphate insecticides in an agroecosystem. Chemosphere 111:623–630

Olaniran AO, Hiralal L, Pillay B (2011) Whole-cell bacterial biosensors for rapid and effective monitoring of heavy metals and inorganic pollutants in wastewater. J Environ Monit 13:2914–2920

Oliveira TMBF, Barroso MF, Morais S et al (2013) Biosensor based on multi-walled carbon nanotubes paste electrode modified with laccase for pirimicarb pesticide quantification. Talanta 106:137–143

Pan Y, Zhou J, Su K, Hu N, Wang P (2017) A novel quantum dot fluorescence immunosensor based on magnetic beads and portable flow cytometry for detection of okadaic acid. Procedia Technol 27:214–216

Peng L, Dong S, Wei W, Yuan X, Huang T (2017) Synthesis of reticulated hollow spheres structure $NiCo_2S_4$ and its application in organophosphate pesticides biosensor. Biosens Bioelectron 92:563–569

Ragavan KV, Selvakumar LS, Thakur MS (2013) Functionalized aptamers as nano-bioprobes for ultrasensitive detection of bisphenol-A. Chem Commun 49:5960–5962

Raliya R, Tarafdar JC (2014) Biosynthesis and characterization of zinc, magnesium and titanium nanoparticles: an eco-friendly approach. Int Nano Lett 4:93. https://doi.org/10.1007/s40089-014-0093-8

Renedo OD, Alonso-Lomillo MA, Martínez MJ (2007) Recent developments in the field of screen-printed electrodes and their related applications. Talanta 73(2):202–219

Rico MA, Olivares-Marín M, Gil EP (2009) Modification of carbon screen-printed electrodes by adsorption of chemically synthesized Bi nanoparticles for the voltammetric stripping detection of Zn(II), Cd(II) and Pb(II). Talanta 80(2):631–635

Rios A, Escarpa A, González MC, Crevillén AG (2006) Challenges of analytical microsystems. Trends Anal Chem 25:467–479

Riu J, Maroto A, Ruis FX (2006) Nanosensors in environmental analysis. Talanta 69:288–301

Romo-Herrera JM, Alvarez-Puebla RA, Liz-Marzan LM (2011) Controlled assembly of plasmonic colloidal nanoparticle clusters. Nanoscale 3:1304–1315

Saha K, Agasti SS, Kim C, Li X, Rotello VM (2012) Gold nanoparticles in chemical and biological sensing. Chem Rev 112:2739–2779

Schulze H, Schmid R, Bachmann T (2002) Rapid detection of neurotoxic insecticides in food using disposable acetylcholinesterase biosensors and simple solvent extraction. Anal Bioanal Chem 372(2):268–272

Selid P, Xu H, Collins EM, Striped Face-Collins M, Zhao JX (2009) Sensing mercury for biomedical and environmental monitoring. Sensors 9:5446–5459

Shankar SS, Rai A, Ahmad A, Sastry M (2004) Rapid synthesis of Au, Ag, and bimetallic Au core Ag shell nanoparticles using Neem (Azadirachta indica) leaf broth. J Colloid Interface Sci 1:1. https://doi.org/10.1016/j.jcis.2004.03.003

Shi H, Zhao G, Liu M, Fan L, Cao T (2013) Aptamer-based colorimetric sensing of acetamiprid in soil samples: sensitivity, selectivity and mechanism. J Hazard Mater 260:754–761

Shitanda I, Irisako T, Itagaki M (2011) Three-electrode type micro-electrochemical cell fabricated by screen-printing. Sensors Actuators B Chem 160:1606–1609

Singh J, Dutta T, Kim K, Rawat M, Samddar P, Kumar P (2018) Green' synthesis of metals and their oxide nanoparticles: applications for environmental remediation. J Nanobiotechnol 16:84

Sinibaldi F, Bongiovanni C, Ferri T, Santucci R (2001) Trends Inorg Chem 7:77–87

Sun D, Xie X, Cai Y, Zhang H, Wu K (2007) Voltammetric determination of Cd^{2+} based on the bifunctionality of single-walled carbon nanotubes-Nafion film. Anal Chim Acta 581:27–31

Sundarmurugasan R, Gumpu MB, Ramachandra BL et al (2016) Simultaneous detection of monocrotophos and dichlorvos in orange samples using acetylcholinesterase-zinc oxide modified platinum electrode with linear regression calibration. Sensors Actuators B Chem 230:306–313

Svancara I, Walcarius A, Kalcher K et al (2009) Carbon paste electrodes in the new millennium. Cent Eur J Chem 7(4):598–656

Tang S, Tong P, Li H, Tang J, Zhang L (2013) Ultrasensitive electrochemical detection of Pb^{2+} based on rolling circle amplification and quantum dots tagging. Biosens Bioelectron 42:608–611

Thakkar KN, Mhatre SS, Parikh RY (2010) Biological synthesis of metallic nanoparticles. Nanomed Nanotechnol Biol Med 6:257–262

Toghill KE, Xiao L, Wildgoose GG, Compton RG (2009) Electroanalytical determination of cadmium(II) and lead(II) using an antimony nanoparticle modified boron-doped diamond electrode. Electroanalysis 21:1113–1118

Tombelli S, Mascini M, Turner A (2002) Improved procedures for immobilization of oligonucleotides on gold coated piezoelectric quartz crystals. Biosens Bioelectron 17(11–12):929–936

Vikesland PJ, Wigginton KR (2010) Nanomaterial enabled biosensors for pathogen monitoring—a review. Environ Sci Technol 44:3656–3669

Vollmer C, Redel E, Abu-Shandi K et al (2010) Microwave irradiation for the facile synthesis of transition-metal nanoparticles (NPs) in ionic liquids (ILs) from metal-carbonyl precursors and Ru-, Rh-, and Ir-NP/IL dispersions as biphasic liquid-liquid hydrogenation nanocatalysts for cyclohexene. Chem A Eur J 16:3849–3858. https://doi.org/10.1002/chem.200903214

Wadhwani SA, Shedbalkar UU, Singh R, Chopade BA (2016) Biogenic selenium nanoparticles: current status and future prospects. Appl Microbiol Biotechnol 100:2555–2566

Wang Q, Fang J, Cao D, Li H et al (2015) An improved functional assay for rapid detection of marine toxins, saxitoxin and brevetoxin using a portable cardiomyocyte-based potential biosensor. Biosens Bioelectron 72:10–17

Wei M, Zeng G, Lu Q (2014) Determination of organophosphate pesticides using an acetylcholinesterase-based biosensor based on a boron-doped diamond electrode modified with gold nanoparticles and carbon spheres. Microchim Acta 181:121–127

Wen L, Lin Z, Gu P et al (2009) Extracellular biosynthesis of monodispersed gold nanoparticles by a SAM capping route. J Nanoparticle Res 11:279–288. https://doi.org/10.1007/s11051-008-9378-z

Yang W, Ratinac KR, Ringer SP, Thordarson P, Gooding JJ, Braet F (2010) Carbon nanomaterials in biosensors: should you use nanotubes or graphene? Angew Chem Int Ed Engl 49:2114–2138

Yang L, Wang G, Liu Y, Wang M (2013) Development of a biosensor based on immobilization of acetylcholinesterase on NiO nanoparticles-carboxylic graphene-nafion modified electrode for detection of pesticides. Talanta 113:135–141

Yildirim N, Long F, He M et al (2014) A portable optic fiber aptasensor for sensitive, specific and rapid detection of bisphenol-A in water samples. Environ Sci Process Impacts 16:1379–1386

Yoosaf K, Ipe BI, Suresh CH, Thomas KG (2007) In situ synthesis of metal nanoparticles and selective naked-eye detection of lead ions from aqueous media. J Phys Chem C 111:12839–12847. https://doi.org/10.1021/jp073923q

Young S, Hart J, Dowman A, Cowell D (2001) The non-specific inhibition of enzymes by environmental pollutants: a study of a model system towards the development of electrochemical biosensor arrays. Biosens Bioelectron 16(9–12):887–894

Yurkov AM, Kemler M, Begerow D (2011) Species accumulation curves and incidence-based species richness estimators to appraise the diversity of cultivable yeasts from beech forest soils. PLoS One 1:1. https://doi.org/10.1371/journal.pone.0023671

Zhang Y, Chen M, Li H et al (2017a) A molybdenum disulfide/gold nanorod composite-based electrochemical immunosensor for sensitive and quantitative detection of microcystin-LR in environmental samples. Sensors Actuators B Chem 244:606–615

Zhang W, Han C, Jia B et al (2017b) A 3D graphene-based biosensor as an early microcystin-LR screening tool in sources of drinking water supply. Electrochim Acta 236:319–327

Zhao Y, Zhang W, Lin Y, Du D (2013) The vital function of Fe_3O_4@Au nanocomposites for hydrolase biosensor design and its application in detection of methyl parathion. Nanoscale 5:1121–1126