

Chapter 9

Nanomaterials in the Development of Biosensor and Application in the Determination of Pollutants in Water



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9.1 Introduction

Recently, nanomaterials have aroused much interest due to the increased need for control and monitoring of different analytes present in samples of environmental relevance (Farré et al. 2011; Pumera 2011; Arain et al. 2018; Liu et al. 2018). A nanomaterial comprises nanoparticles (NPs) that are less than 100 nm at least in one

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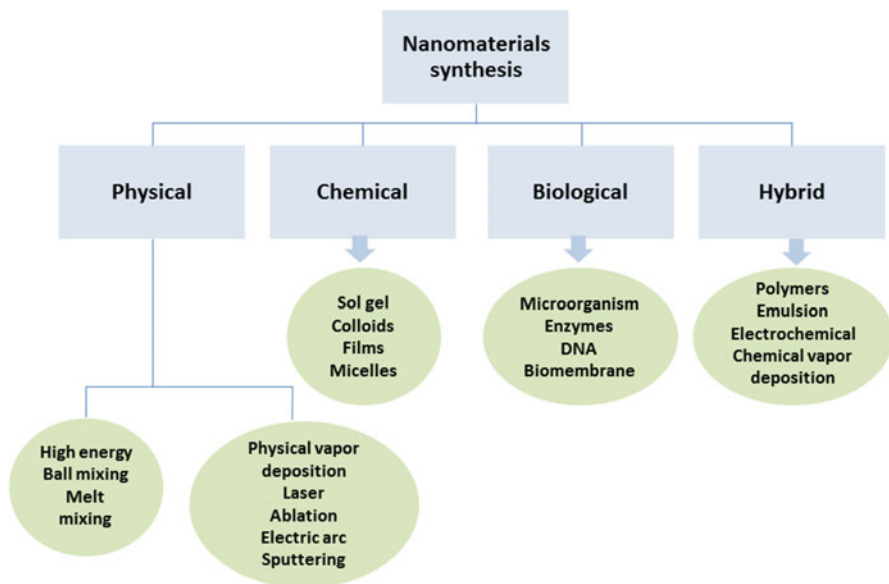


Fig. 9.1 Scheme of different methods that can be used for the nanomaterials synthesis

dimension (Gajanan and Tijare 2018). The controlled synthesis and tuning properties of nanomaterials require knowledge of different disciplines such as physics, chemistry, electronics, computer science, biology, medicine, engineering, agriculture, and others that may lead to the emergence of novel and multifunctional nanotechnologies (Gajanan and Tijare 2018). Various methods can be used to synthesize nanomaterials in different forms such as colloidal NPs, metallic NPs, nanoclusters, nanopowders, nanotubes, nanorods, nanowires, and thin films, among others (Mackenzie and Bescher 2007). The conventional methods with some modification can be utilized to obtain nanomaterials (Hasan et al. 2018). Figure 9.1 shows a flow chart of different methods that can be utilized for the synthesis of nanomaterials. The physical, chemical, biological, and hybrid methods have been developed for the nanomaterials synthesis (Prasad et al. 2016; Choi et al. 2007; Hasan et al. 2018). The selection of a synthesis method depends on the material of interest or the type of nanomaterial, their sizes, and the desired quantity (Zhang and Wei 2016; Hasan et al. 2018). Besides, bottom-up and top-down are the main approaches for synthesis of nanomaterials (Hasan et al. 2018; Liu et al. 2018). Bottom-up is an approach in which the miniaturization of material elements (atomic level) followed by self-assembly results in the creation of nanostructures (Hasan et al. 2018). Moreover, during the self-assembly process, the basic unit of a larger structure is composed of nanomaterials (Lan et al. 2017; Hasan et al. 2018). This approach yields lesser defects and a more homogeneous chemical composition (Arlett et al. 2011; Hasan et al. 2018). On the other hand, in the top-down approach, the large (macroscopic) structure can be externally controlled during processing of the desired nanomaterials (Luo et al. 2009; Hasan et al.

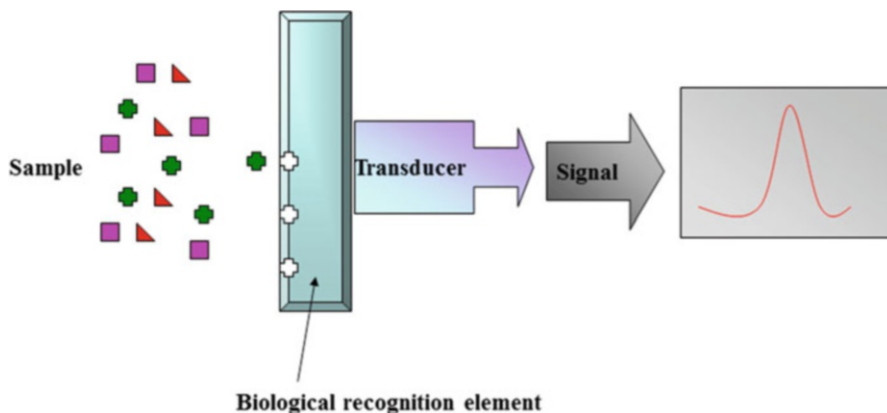


Fig. 9.2 Schematic representation of the biosensor. This device comprises three main components: a sensitive biological recognition element, a transducer, and a signal processor

2018). A major drawback in this approach is the presence of imperfections in the surface structure. Surface defects in this approach can have an impact on physical and surface properties of NPs due to the high aspect ratio (Hasan et al. 2018; Maduraiveeran et al. 2018). In this context, the exciting properties of nanomaterials have attracted the world scientific community toward their application in various sectors such as health, food, security, transport, and information technology (Luo et al. 2009; Hasan et al. 2018; Prasad et al. 2014, 2017; Aziz et al. 2015, 2016). The intelligent use of nanomaterials is predicted to enhance the performance of miniaturized biosensor-based devices with high sensitivities and detection limits (Choi et al. 2007; Luo et al. 2009; Li et al. 2015a, b, c, d; Kurbanoglu et al. 2017; Maduraiveeran et al. 2018; Faraz et al. 2018).

A biosensor is a miniaturized analytical device that integrates a biological element on a solid-state surface which enables a reversible biospecific interaction with the analyte, and a signal transducer (Turner et al. 1987) (Fig. 9.2). The biological element is a layer composed of molecules qualified for biorecognition, such as enzymes, receptors, peptides, antigens, antibodies, single-stranded DNA, even living cells are applicable (Tansil and Gao 2006; Arlett et al. 2011). If antibodies or antibody fragments are applied as the biological element, the device is called immunosensor (Bravo et al. 2017; Piguillem et al. 2018). Many devices are connected with a flow-through cell, enabling a flow injection analysis (FIA) mode of operation (Fernández Baldo et al. 2009). Biosensors combine high analytical specificity with the processing power of modern electronics components to achieve highly sensitive detection systems (Fernández Baldo et al. 2009). There are two different types of biosensors: biocatalytic and bioaffinity-based biosensors (Regiart et al. 2017). The biocatalytic biosensor uses mainly enzymes as the biological compound, catalyzing a biochemical signaling reaction (Regiart et al. 2017). The bioaffinity-based biosensor, designed to monitor the binding event itself, uses specific binding proteins, lectins, receptors, nucleic acids, membranes, whole cells, or antibodies for biomolecular recognition

(Bravo et al. 2017). Biosensors technology seeks to improve analytical performance by reducing the consumption of reagents, decreasing the analysis time, increasing reliability and sensitivity through automation, and integrating multiple processes in a single device (Regiart et al. 2017).

Recently, some biosensors for the pollutants in water samples determination have been fabricated using incorporated nanotechnology (Xu et al. 2013; Wang et al. 2013; Devasenathipathy et al. 2014; Lai et al. 2014; Wei et al. 2014; Chamjangali et al. 2015; Li et al. 2015a, b, c, d; Sun et al. 2015; Bapat et al. 2016; Hayat et al. 2016; Ramnani et al. 2016; Zeng et al. 2016; Mishra et al. 2017; Scala-Benuzzi et al. 2018a). These kinds of novel devices have a high speed of response, accuracy, lower cost, and less operator intervention (Bidmanova et al. 2016; Jarque et al. 2016). Others advantages of these analytical methods are the reduction of the amount of solvents and reagents required in sample pretreatment as well as in the measurement steps (Regiart et al. 2017). These benefits are the consequence of the automation and miniaturization which reduced the adverse environmental impact of analytical methodologies (Fernández Baldo et al. 2009). Besides, the use of some nanomaterials (quantum dots, carbon nanotubes, magnetic and metallic nanoparticles) as a bioaffinity platform for the immobilization of biomolecules or electrode modification had permitted the development of biosensors with enhanced sensitivities and improved response times (Zhang and Wei 2016; Maduraiveeran et al. 2018). This chapter focuses on the application of biosensors with incorporated nanotechnology in the determination of pollutants in water samples.

9.2 Relevant Characteristics of Nanomaterials

Nanomaterials are currently undergoing rapid development due to their potential applications in the field of nanoelectronics, catalysis, magnetic data storage, structural components, biomaterials, and biosensors (Maduraiveeran et al. 2018). In the last years, the use of NPs, nanotubes, and nanowires in biosensor diagnostic devices are being explored (Lan et al. 2017; Liu et al. 2018). With the advancement in properties of nanomaterials, their dimensions at the nanoscale level, new biodevices (smart biosensors) that can detect minute concentration of a desired analyte are emerging (Liu et al. 2018). Nanomaterials are generally used as transducer materials that are an important part for biosensor development (Lan et al. 2017). Also, these nanomaterials are used as such as bioaffinity platform for the immobilization of biomolecules (DNA, enzymes, antigens, or antibodies) or for electrode modification in the development of biosensors (Zhang and Wei 2016; Bravo et al. 2017). The engineered nanomaterials provide higher electrical conductivity, have nanoscale size, can be used to amplify desired signals, and are compatible with biological molecules (Zhang and Wei 2016). For example, carbon materials can be utilized for conjugation of biomolecules (enzyme, antibody, DNA, or cell) (Fernández Baldo et al. 2009). It has been found that the use of nanomaterials may lead to increased biosensor performance including increased sensitivities and low limit-of-detection of

several orders of magnitudes (Bravo et al. 2017; Regiart et al. 2017). Therefore, nanostructured materials show increased surface-to-volume ratio, chemical activity, mechanical strength, electrocatalytic properties, and enhanced diffusivity (Piguillem et al. 2018). Nanomaterials have been predicted to play an important role toward the high performance of a biosensor (Bravo et al. 2017). To probe biomolecules such as bacteria, virus, or DNA, biocompatibility of nanomaterials is an important factor for designing a biosensor (Maduraiveeran et al. 2018). Furthermore, a variety of samples such as body fluids, environmental samples, food samples, and cells culture can be explored to analyze using biosensors with incorporated nanomaterials (Kurbanoglu et al. 2017).

9.3 Nanomaterials Used in Biosensors Methodologies

Several nanomaterials have been used for the biosensors development in view of their excellent optical, electronic, thermal, and mechanical properties. They are recognized as one of the most interesting materials for the design of next-generation biosensors. With their high surface area to volume ratio, excellent magnetic, great electronic conductivity, and physicochemical properties (Maduraiveeran and Jin 2017), different kinds of nanomaterials (including metal nanomaterials, carbon nanomaterials, magnetic nanoparticles, silica nanoparticles, up-conversion nanoparticles, and quantum dots, between others) have been successfully applied to develop various biosensors for target analytes detection, like several contaminants in water (Zeng et al. 2016). Table 9.1 summarizes and compares the most relevant articles related about nanomaterials used in biosensors fabrication for the pollutants determination in water. In this section, the basic properties of these types of nanomaterials used in biosensors are discussed.

9.3.1 Carbon Nanomaterials

Carbon nanomaterials, including carbon nanotubes, carbon nanofibers, fullerene, graphene quantum dots, graphene, and micro/meso/macro porous carbon, are obtaining a high consideration for their extraordinary properties (Wang and Dai 2015; Yang et al. 2015). Among them, carbon nanotubes, graphene, and porous carbon are the most frequently used carbon nanomaterials in biosensors for contaminants detection in water (Ramnani et al. 2016).

9.3.1.1 Carbon Nanotubes

Carbon nanotubes (CNTs), one-dimensional carbon nanomaterials, are sp^2 hybridized carbon atom rolled graphene sheets that were discovered by Iijima in 1991

Table 9.1 Nanomaterials used in biosensors fabrication for the pollutants determination in water

Analytes	Nanomaterials	Detection methods	Sample	Refs.
Herbicide MCPA	β -CD/MWNTs	CV	Natural water	Rahemi et al. (2012)
Dichlorvos	MWNTs/ALB	CV	Water	Yan et al. (2013)
Olaquinox	MWNTs	DPV	Water	Xu et al. (2013)
Cd^{2+}	MWNTs	DPV	Water	Afkhami et al. (2014a, b)
Cd^{2+}	MWNTs/PPCV/Bi	DPV	Water	Chamjangali et al. (2015)
Cu^{2+}	MWNTs/GCE	NPASV	River water	Liang et al. (2014)
Thiocyanate	AuNPs/MWCPE	SWV	Water	Afkhami et al. (2014a, b)
Hydroquinone	rGO–MWNTs	DPV	River water	Hu et al. (2012)
Phoxim	P3MT/NGR	CV	River water	Wu et al. (2015)
Isoproturon carbendazim	GR	SWSV	Water	Noyrod et al. (2014)
Imidacloprid	GO	CV	Lake water	Lei et al. (2014)
Napropamide	Sulfonated GR	ECL	Water	Wang et al. (2014a, b)
Pb^{2+}	GQDs	ECL	Water	Dong et al. (2014)
Cd^{2+}	Sn/poly(<i>p</i> -ABSA)/GR	SWASV	Water	Wang et al. (2014a, b)
Nitrite	Au-rGO/PDDA	DPV	Lake water	Jiao et al. (2015)
Nitrite	GC–GNs–Th	AM	Water	Shervedani et al. (2016)
SO_3^{2-}	GR-CS/AuNPs GCE	AM	Water	Wang et al. (2013)
Hydrazine	GR/CCLP-AuNPs	AM	Water	Devasenathipathy et al. (2014)
Hydroquinone	CFG	DPV	Sea water	Li et al. (2015a, b, c, d)
Hydroquinone	PEDOT/NGE	DPV	Lake water	Si et al. (2014)

(continued)

Table 9.1 (continued)

Analytes	Nanomaterials	Detection methods	Sample	Refs.
Anthracene	GR-PANI	SWV	Water	Tovide et al. (2014)
Thiols	NGR/CoPc	AM	Water	Xu et al. (2015)
Nitrite	Fe ₃ O ₄ -MWNTs PhCOOH	DPV	Water	Pistone et al. (2013)

CV cyclic voltammetry, *DPV* differential pulse voltammetry, *SWV* square-wave voltammetry, *SWSV* square wave stripping voltammetry, *SWASV* square-wave anodic stripping voltammetry, *AM* amperometric, *NPASV* normal pulse anodic stripping voltammetry, *β -CD* β -cyclodextrin, *ALB* AChE liposomes bioreactor, *NPs* nanoparticles, *GNs* graphene nanosheets, *GR* graphene, *GO* graphene oxide, *MWCPE* multi-walled carbon nanotube/carbon paste electrode, *NGR* nitrogen-doped graphene, *PPCV* poly(pyrocatechol violet), *PDDA* poly(diallyldimethylammonium chloride), *rGO* reduced graphene oxide, *CFG* carboxyl functionalized graphene, *GQDs* graphene quantum dots, *AuNPs* Au nanoparticles, *PANI* polyanilino, *CCLP* calcium ions cross linked pectin film, *PEDOT* poly(3,4-ethylenedioxythiophene), *CoPc* cobalt phthalocyanine, *P3MT* poly(3-methylthiophene), *MWNTs PhCOOH* MWNTs chemically functionalized with the benzoic acid group

(Iijima 1991). These can be classified into single wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs), according to the number of rolled layers. Since their discovery, NTs have an increased attention due to their unique thermal, electronic, and mechanical properties. In this way, their great mechanical flexibility, unique thermal conductivity, excellent electrochemical stability, and fast electron transfer make them a unique material for the application in biosensors (Tilmaciu and Morris 2015; Lawal 2016). To improve their solubility and biocompatibility, CNTs can be functionalized with carboxyl or amino groups or form combinations with other materials, such as polymers, ionic liquids, or metal nanoparticles. Chemical groups are able to connect with biomolecules (e.g., antibodies and/or enzymes) or organic molecules (Besteman et al. 2003; Balasubramanian and Burghard 2006). In the last decades, CNTs-based biosensors have been extensively used for the detection of contaminants in water (Xu et al. 2013; Wei et al. 2014).

9.3.1.2 Graphene

Graphene (G), two-dimensional carbon nanomaterials, is a sheet of sp² bonded carbon atoms that are arranged into a rigid honey comb lattice, exhibiting the highest mechanical strength between know materials, excellent electrical conductivity, large specific surface area, high electron transfer capabilities, exceptional pliability and impermeability, and good biocompatibility (Wang et al. 2016a, b). Since its discovery in 2004, graphene has been successfully applied into various fields, such as energy storage, catalysis, sensor, and electronic devices. In addition, graphene can be easily oxidized into graphene oxide (GO), which contains many hydrophilic groups such as carbonyl, epoxy, hydroxyl, and carboxyl groups (Lei et al. 2014; Vilian et al. 2014). These hydrophilic groups make GO aqueous dispersibility and

easy to be functionalized with biomolecules (e.g., antibodies, enzymes), which are highly important features in biosensor applications (Si et al. 2014; Wu et al. 2015).

9.3.1.3 Porous Carbon

Porous carbon with a high surface area, accessible surface chemistry, and short pathway for mass and electron transfer has attracted considerable attention due to the promising applications in biosensors, especially in electrochemical biosensors. Jun et al. (2000) synthesized the first nanostructured carbon type CMK-3. They used an ordered mesoporous silica material (SBA-15) and sucrose as a carbon source. The resulting material was a negative replica of the porous structure of SBA-15 formed by interconnected carbon nanorods. This material became attractive due to its interesting textural, structural, and morphological properties. Compared to the corresponding template, the nanostructured carbons exhibit a hydrophobic nature, excellent mechanical strength and thermal stability, thus becoming a material of great interest for several applications (Niu et al. 2016; Regiart et al. 2016). According to the International Union of Pure and Applied Chemistry (IUPAC) recommendation, porous carbon materials can be grouped into three classifications based upon their pore sizes: microporous <2 nm, 2 nm $<$ mesoporous <50 nm, and macroporous >50 nm (Lee and Hyeon 2006).

9.3.2 Metal Nanoparticles

Metal nanoparticles (NPs) are a class of functional materials with unique chemical and physical properties, which are closely related to their shape, structure, composition, and size. Great progress has been made in the synthesis of NPs and their potential applications in innumerable fields such as in electronics, sensors, catalysis, and medicine (Han et al. 2017; Kangkamano et al. 2017; Faraz et al. 2018; Prasad et al. 2016). Because of their excellent electron transfers kinetics, high specific surface area, and plenty absorption sites to enzymes, antigen, and antibodies. NPs have attracted a great consideration in the biosensors development for water contaminants detection (Devasenathipathy et al. 2014).

9.3.2.1 Gold Nanoparticles (AuNPs)

Significant efforts have been made on the development of biosensor platforms based on Au nanoparticles for environmental applications due to the unique properties such as high surface area, outstandingly tunable optical properties, and capability for the surface modification (Lv et al. 2018). AuNPs open the possibility for the miniaturization of sensing devices to the nanometer scale, which offer excellent chemical sensing prospects. Nanoscale electrochemical biosensor based on Au via

micro and nanofabrication technologies offer a marvelous impeding for the development of biosensor array platforms for the environmental pollutants detection. In recent years, the integration capability of the biosensor arrays with microfluidic devices provides possibilities for lab-on-a-chip technology for the sensing of multiple analytes in a high-throughput approach (Wolfrum et al. 2016). AuNPs based modified electrodes or nanosized electrodes offer numerous advantages such as higher signal-to-noise ratio (S/N), high selectivity, and improved catalytic activity and diffusion of electroactive species. In addition, AuNPs possess a unique phenomenon called as surface plasmon resonance, in which any change/alteration in the size, shape, or geometry of particles alters the local electron confinement that is thereby reflected in the absorption maxima and color of colloidal solution (Saha et al. 2012). These properties are significant in the development of various biosensors for contaminants detection in water samples (Wang et al. 2013).

9.3.2.2 Silver Nanoparticles (AgNPs)

Owing to the high conductivity, amplified electrochemical signal, and excellent biocompatibility, the development of the AgNPs based biosensor has made significant impact for environmental applications. Over last two decades, extensive work has been made toward the design of novel analytical methods based on AgNPs and their nanocomposites for food safety and environmental monitoring (Zhai et al. 2015). It has been succeeded that the AgNPs have been recognized as one of the outstanding groups of the nanomaterials for biosensing methods. AgNPs based electrode materials have unlocked up the opportunity of generating new analytical platforms for emerging environmental organic, inorganic, and biological pollutants due to their high sensitive and specific nature (Li et al. 2015a, b, c, d). The incorporation of the AgNPs into numerous matrixes such as metal oxides, silicate network, polymers, graphene, fibers, and dendrimers provides enhanced sensing performance with high stability because of the extended utility of the materials. The stability and sensitivity of the biosensor platform relate to the dispersion and the prevention of the aggregation process of the AgNPs in the network. AgNPs are stabilized via steric repulsion and electrostatic repulsion of the stabilizing agents with polymers or other matrices.

9.3.3 Metal Oxide Nanoparticles

Metal oxides nanoparticles with large surface area, exceptional electrochemical activity, high adsorptive capacity, and stability are of great significance for biosensor platforms design (Regiart et al. 2015; Wu et al. 2016). The analytical performance of the metal oxide nanoparticles based biosensors can be well tuned by tailoring the properties of the particle size, morphology, surface functionality, and surface area.

9.3.3.1 Metal Oxides Nanoparticles

For the synthesis of metal oxides nanoparticles, chemical methods including reduction of metal ions and controlled separation of the formed metal atoms from the bulk solution were developed. They are quite advantageous to obtain uniform nanostructures, such as nanorods, nanofibers, nanobelt, nanocomb, and nanotubes. This family of one-dimensional nanostructures provide a great model system for sensing of environmental pollutants. Biosensors based on nanoscale metal oxide semiconductors such as CuO, ZnO, NiO, and TiO₂ play an important role in the environmental monitoring of water contaminants (Wei et al. 2012; Hayat et al. 2016). In order to increase the detection limit and sensitivity, considerable labors have been performed on the design and controllable synthesis of the hierarchical metal oxides nanostructures due to their smaller size and characteristic charge carriers.

9.3.4 Magnetic Nanoparticles

Magnetic nanoparticles (MNPs) have improved a growing attention in the development and applications of biosensors in the last years. Huge efforts have been made to develop MNPs because of their particular characteristics such as high mass transference, large surface area, biocompatibility with biomolecules, unique physicochemical properties, and easy production (Akbarzadeh et al. 2012; Reddy et al. 2012). MNPs display superparamagnetic property below 50 nm size and perform best from 10 to 20 nm, making them a suitable choice in magnetic fields when quick response is required. Moreover, MNPs are able to be incorporated into microfluidic biosensors, attracting analytes in the samples by an external magnetic field (Netto et al. 2013; Rocha 2014). Compared to non-MNPs-based strategy, biosensing strategy based on MNPs has many advantages including lower detection limit, improved sensitivity, and faster analysis times (Justino et al. 2013). In the last years many biosensors using magnetic nanoparticles for water contaminants determination were published (Lai et al. 2014; Sun et al. 2015).

9.3.5 Up-Conversion Nanoparticles

Up-conversion nanoparticles (UCNPs) are a novel class of luminescent materials that transform the near-infrared radiations (lower energy) into visible radiation (higher energy) (Wang et al. 2011). It has been paid significant attention in various fields due to their low toxicity, low background noise, high photo stability, and great penetration of signals in tissues with low absorption (Zhang et al. 2016). These advantages make them a better choice in comparison to down conversion fluorescent

materials, such as organic fluorescent dyes and inorganic quantum dots. Generally, they are used as fluorescent labels combined with biorecognition molecules (e.g., enzymes, antibodies) for water contaminants detection in optical biosensors (Wang et al. 2005).

9.3.6 *Quantum Dots*

As semiconductor nanocrystals, quantum dots (QDs), including ZnS, CdS, and CdTe, display exceptional electronic and optical properties, such as long-term photo stability, high luminescence, broad absorption bands, resistance to photo-bleaching, size-tunable, narrow, and symmetric emission (Bonilla et al. 2016), which make QDs very attractive in analytical chemistry. Moreover, QDs provide the suitability of aptamer/antibody conjugation without affecting either their emission properties or aptamer/antibody specificity (Stanisavljevic et al. 2015).

9.3.7 *Silica Nanomaterials*

In recent decades, many porous materials have been developed, but the synthesis of ordered porous materials is one of the most important advances in the field of materials science. In the early 1990s, researchers from the Mobil Oil Corporation reported the synthesis of the first M41S family (MCM-41 and MCM-48). Another interesting family of these mesostructured silica particles was developed in 1998 by researchers from the University of California, in Santa Bárbara, denominating them SBA (SBA-15 and SBA-16) (Kresge et al. 1992; Zhao et al. 1998).

Functionalized silica based particles such as nanoporous silica, silica nanofibers, silica nanotubes, and silica coated magnetic nanoparticles have been reported for water contaminants detection (Bapat et al. 2016; Mishra et al. 2017). Silica materials can be modified with amino and carboxyl groups, among others, by functionalization and impregnation. The amino functionalization can be carried out by means of: (a) direct synthesis or co-condensation, a method consisting of the joint condensation of the silica precursor (tetraethylorthosilicate, TEOS) and the organosilane compound having one or more amino groups. (b) Anchoring, a method that consists of the covalent union of organosilane compounds with the Si–OH (silanol) groups found on the surface of the wall of the silica material. (c) Anchoring with thermal ammonolysis, a method that consists of substituting the –OH surface groups for amino groups (–NH₂) by means of a thermal treatment in the presence of NH₃. On the other hand, they can be modified by impregnation of the silica with amino compounds such as monoethanolamine (MEA), diethanolamine (DEA), and polyethyleneimine (PEI), among others (Regiart et al. 2017).

9.3.8 *Polymer and Biomaterials*

Polymer and biomaterials based biosensor have several advantages, like rapid response, improved sensitivity, and selectivity due their electrical, radiant, mechanical, thermal, physical, and catalytic properties (Yang et al. 2016). The design and the development of biosensor for detecting environmental pollutants in water based on polymeric biomaterials with unique functionalities and properties can be presently accomplished by combining the novel analytical and scientific methods, including high-throughput materials screening with micro/nanofabrication, and microfluidics (Wang et al. 2016a, b).

9.3.8.1 **Polymer Materials**

The development of polymeric materials, including homo and copolymers, formulated materials, polymeric structures with engineered morphology, and molecular shape recognition materials has been established for the sensitive biosensing of environmental pollutants in water (Chamjangali et al. 2015). The polymeric materials have exhibited several properties, including linearity, sensitivity, ease of produce, and selectivity. The formation of self-assembled biomembranes, electropolymerized polymers, and dendrimers based polymeric materials has motivated extensive dedication in the design of biosensors. Synthetic organic polymers or biopolymers, such as cellulose and chitosan, have polyfunctional groups in their surface like $-\text{NH}_2$, $-\text{OH}$, $-\text{COOH}$, etc. (Tehrani et al. 2013). However, the small surface area and slow adsorption rate limit their application. Meanwhile, metal nanoparticles or carbon materials have large surface area, and can be functionalized with chemical groups in the surface, improving the biocompatibility, sensitivity, and selectivity in the determination (Wang et al. 2013).

9.3.8.2 **Biomaterials**

The integration of biomolecules with nanocomposites combines the great characteristics of nanomaterials and biomolecules. Functional group in nanocomposites can be coupled with biomolecules like enzymes or antibodies. Due to the unique recognition, transport, electronic and catalytic properties, the biomaterials offer highly selective catalytic and recognition properties (Sabela et al. 2016). Polymer nanocomposites have large surface areas and multifunctional groups in the surface compared to metal/oxide nanoparticles, activated carbon, and organic polymers. Polymer biomaterials include polymer nanoparticles, polymer nanofibers, polymer nanocrystals, and polymer nanorods. The development and application of polymer biomaterials provides an alternative opportunity for the efficient detection of contaminants in water (Li et al. 2015a, b, c, d).

9.4 Recent Developments Applied to Pollutants Determination in Water Samples

The pollution of air, water, and other natural resources is a major global concern generated by the industrialization and urbanization in the last decades (Ramnani et al. 2016).

This fact increased the demand for strict testing and controlling of harmful substances in water resources. Traditionally, this monitoring requires time-consuming analyses, skilled personnel and laboratories equipped with sophisticated instrumentation. For these reasons the development of rapid, low-cost, and easy-to-use point-of-need detection tools can play an important role in preventing and/or minimizing diseases associated to polluted water (Sharma et al. 2015).

Hydroquinone, catechol, and resorcinol are considered as priority pollutants by US Environmental Protection Agency (EPA) and the European Union (EU) due to their genotoxicity, carcinogenicity, and toxicokinetic effect on humans. For these reasons, an electrochemical sensor for its determination in water samples has been developed using Nafion, multi-walled carbon nanotubes, and carbon dots (Wei et al. 2014).

The functionalized MWCNTs containing amido bond offer sizeable specific surface area, while carbon dots containing carboxyl groups have electrical conductivity. These materials were combined through electrostatic interactions for the composite obtention and used for the electrode modification procedure with the aid of Nafion which protect the electrode modification. This system was applied to the determination of mentioned pollutant compound on tap water, well water, and river water samples showing adequate stability and sensitivity.

Organophosphorus pesticides represent another kind of important water pollutant, which are globally distributed, due to its use in the enhancement of agricultural production. They are known because of their effect as an acetylcholinesterase inhibitor. Mainly, chlorpyrifos (*O, O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl)-phosphorothioate), one of the pesticides most often used, could generate harmful effects on central nervous, cardiovascular, and respiratory systems. Sun et al. (2015) developed an electrochemical immunoassay for the quantitative detection of chlorpyrifos using carbon nanotubes, polydopamine, and Fe₃O₄ shell. In the development of this sensor polydopamine was used as nanospheres in the modification of electrode surface and for the modification of carbon nanotubes which after a co-precipitation process of Fe²⁺ and Fe³⁺ in the presence of ethylene glycol generated a flake-like Fe₃O₄ coated carbon nanotubes (CNTs@f-Fe₃O₄). This nanocomposite was used as the carrier of the multi-enzyme label due to its capacity of loading the secondary antibody and horseradish peroxidase (HRP). The synthesized material was exhaustively evaluated by different characterization techniques and applied on the chlorpyrifos determination on water samples from lakes and the pond water from farmland. The high sensitivity reached was attributed to the large surface area of the flaky morphology for loading abundant of antibodies and HRP.

Methyl parathion (MP) is another organophosphate that is used as a non-systemic insecticide in agriculture. For its quantification in real and spiked water samples, Mishra et al. (2017) have proposed an optical microplate biosensor using a biohybrid

of *Sphingomonas* sp. cells with modified SiNPs. In their study, SiNPs were functionalized with PEI (fSiNPs), and they were integrated with *Sphingomonas* sp. cells culture for obtaining a Biohybrid of *Sphingomonas* sp. -fSiNPs. The Biohybrid was immobilized on a microplate and associated directly with the optical transducer of the microplate reader. The authors demonstrated that the integration of fSiNPs with *Sphingomonas* sp. improved the sensitivity and stability of the biosensor more than ten times.

Herbicides used in agricultural production as linuron, 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea] (Chen and Zhu 2015) have been quantitatively determined by a new method of magnetic solid phase extraction (MSPE) coupled with UV spectrometry for separation/quantitation of linuron. The authors used three hydrophobic ionic liquids (ILs), including 1-butyl-3-methylimidazole hexafluorophosphate, 1-hexyl-3-methylimidazole hexafluorophosphate, and 1-octyl-3-methylimidazole hexafluorophosphate for coated $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles with core-shell structure to prepare magnetic solid phase extraction agent ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{ILs}$). Linuron was adsorbed by $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{ILs}$ and eluted by ethanol. This proposed method has been successfully applied for the determination of linuron in water lake samples.

In the last decades, growth promoters have been extensively used to improve feed efficiency. Olaquinox (OLA;2-(*N*-2-hydroxyethylcarbamonyl)-3-methyl-quinoxaline-*N*1, *N*4-dioxide), belongs to this group of agents and has been founded as a pollutant in water samples. Its carcinogenic and genotoxic effects have been established in several studies. In Xu et al. (2013) the design and construction of an electrochemical sensor based on the modification of the electrode surface with multi-walled carbon nanotubes was described. This system was applied to analyze synthetic and real fishery water samples showing a high sensitivity due to multi-walled carbon nanotubes remarkably enhance the reduction of and consequently improved the cathodic peak current.

Sulfite (SO_3^{2-}) is widely used as a bleaching agent and an antioxidant in the food industry, while nitrite (NO_2^-) is used as a coloring agent and preservative. Both chemical agents usually coexist in the atmosphere and water. The sulfite excess generates the irreversible oxidation of the hemoglobin and nitrite can react with amines to form carcinogenic nitrosamine. In Wang et al. (2013), the simultaneous determination of SO_3^{2-} and NO_2^- was carried out using an electrochemical sensor with a glassy carbon electrode modified with graphene, chitosan, and gold nanoparticles. The results for SO_3^{2-} and NO_2^- determination in water samples obtained from a park, school, and rain using the mentioned system showed many advantages. Among them, electrochemical catalytic activity attributed to the small size and surface effect of graphene which could enhance the redox activity of SO_3^{2-} and NO_2^- and reduce the charge transfer resistance. Besides, chitosan polymer has positive charges in acidic solutions attracting negatively charged ions (SO_3^{2-} and NO_2^-). Moreover, the gold nanoparticles increase the contact area for the catalytic reaction but also provides a path for electron transfer and the catalytic process.

Additionally, Sudha et al. (2018), reported the construction of a modified electrode with COOH-functionalized with multiwall carbon nanotubes for simultaneous estimation of sulfite and nitrite in underground and pond water samples. HOOC-

MWCNT characterization demonstrated the discrete tube morphology of it which improved the active surface area enhancing the response for SO_3^{2-} and NO_2^- .

The excess of heavy metals can cause various health problems. Particularly Lead generates harmful effects for humans, including physiological, biochemical, and genetic dysfunctions. Based on the interaction of Pb (II) ions with nucleic acid via phosphate groups and nucleic bases of the deoxyribonucleic acid structure, Lian et al. (2014) have proposed a high selectivity electrochemical sensor with DNA wrap metallic single-walled carbon nanotube (SWNT) for quantitation of Pb^{2+} . The response of Pb^{2+} in river water samples was investigated by differential pulse voltammetry (DPV). The author had demonstrated that metallic SWNTs played an important role in enlarging current response and increased sensitivity of the sensor.

Emerging pollutants are residues of human activity such as personal care, healthcare, and industrial operations. There is no regulation on their presence and levels in the environment. Among them, the endocrine disrupting compounds (EDCs) are related to some health problems. Ethinylestradiol (EE2) is a synthetic hormone with high estrogenic potency and is one of the main components of oral contraceptives. EE2 has become an emerging pollutant in aquatic ecosystems because it is resistant to degradation by the liver. Therefore, EE2 and its derivatives are introduced into the environment via wastewater. For the quantitation of EE2 in different water sources samples, paper-based immunosensors had been recently proposed. Scala-Benuzzi et al. (2018b) have developed a fast and sensitive paper-based analytical device coupled to LED-induced fluorescence detection (FPAD) for the quantification of EE2 in river water samples. The FPAD was based in a competitive enzyme immunoassay format. Paper microzones were modified with amino-functionalized SBA-15, and subsequently anti-EE2-specific antibodies were covalently immobilized. The determination of EE2 in water samples was carried out by adding a fixed concentration of EE2-conjugated HRP to samples and standards. Also, a novel and innovative electrochemical paper-based immunocapture assay (EPIA) for the highly sensitive detection of EE2 were presented by Scala-Benuzzi et al. (2018a). The EPIA approach was based on the use of paper microzones modified with SiNPs and anti-EE2-specific antibodies for capture and preconcentration of EE2 from river water samples. Recovered EE2 was electrochemically detected by OSWV using an SPCE modified with electrochemically reduced graphene (RG).

Besides, Martinez et al. (2012) have developed an accurate, sensitive, and selective method for capture, preconcentration, and determination of EE2 present in water samples using MPs as bioaffinity support for the capture and preconcentration of EE2 and a glassy carbon electrode modified with MWCNTs/GCE as the detection system. The capture of EE2 from water samples was based on the principle of immunoaffinity, and the determination of the pre-concentrated EE2 was carried out by square wave voltammetry (SWV).

Phenolic compounds could also generate endocrine disruption effect. Hayat et al. (2016) developed an SPCE modify with TiO_2 /activated carbon nanocomposite for the detection of four phenolic endocrine disruptors in water samples. The modified SPCE showed advantageous characteristics regarding electro conductivity, catalytic

activity, and surface area in comparison with an unmodified SPCE. The modified transducer surface was successfully used for the detection of four phenolic endocrine disruptors, *p*-nitrophenol, hydroquinone, catechol, and 1-naphthol in river water samples.

9.5 Conclusions

Nanomaterials for biosensor development applied for pollutants determination in water samples are discussed in this chapter. An important challenge is the standardization of immobilization procedure that can be utilized to intimately conjugate a biomolecule onto a nanomaterial or for the electrode modification with a nanomaterial. Therefore, the technique used to immobilize a given biomolecule or electrode modification is one of the factors more relevant in developing a reliable biosensor with relevant applications. A nanomaterial can be an excellent candidate to immobilize biomolecules on a transducer surface that can efficiently maintain bioactivity of these biomolecules. Finally, there are still many challenges such as miniaturization, automation, and integration of the nanostructured-based biosensors.

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