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Chapter

The Novel Nanomaterials Based Biosensors and Their Applications

Kübra Gençdağ Şensoy and Mihrican Muti

Abstract

Since the development of the first biosensor reported, biosensor has received considerable attention due to its high selectivity and sensitivity. Biosensors are highly pursued in order to meet the growing demands and challenges in a large number of analytic applications such as medical diagnosis, food safety control, environmental monitoring, or even military defense. Due to the unique physical, chemical, mechanical and electrical properties, nanomaterials have been widely investigated for their ability and used to fabricate sensors. High surface to volume ratio, good stability, excellent electrocatalytic properties of the nanomaterials plays an important role in the sensitive and selective detection of biomolecules. The synthesis of new nanomaterials with different properties is increasingly common in order to improve these counted properties of nanomaterials. This chapter gives an overview of the importance of the development of novel nanomaterials based biosensors technologies. The use of different funtionalized carbon nanomaterilas, metal oxide nanoparticles, metal nanoparticles, polymeric nanoparticles, quantum dots, graphene sheets and other novel nanomaterials in biosensor technology, and their innovations and advantages are discussed.

Keywords: novel nanomaterials, biosensor, biorecognition, nanosensors

1. Introduction

A biosensor device is defined as a biological or bio-inspired receptor unit with unique specificities for analytes. These analytes are generally of biological origin. One of the challenges in biosensor development is that efficient signal capture can be achieved with biological recognition. Novel nanomaterials represent a rapidly developing field in bioanalysis applications. The sensitivity and performance of biosensors can be improved by using nanomaterials. Typical schemeatic presentation of a biosensor is illuatrated in **Figure 1**.

With the development of nanotechnology, many new nanomaterials such as gold nanostructure, magnetic nanoparticles, nanozymes, and carbon-based nanomaterials have been synthesized [1]. Nanomaterials have been widely applied in the areas of invivo imaging [2], cancer treatment [3], drug delivery [4], catalysis [5], bacteriostasis [6], and so on. Due to the outstanding physical and chemical properties of nanomaterials, nanomaterial-based biosensors have been developed [7].

In this chapter, synthesis, properties and possible applications of these materials in biosensors were examined. The high sensitivity and selectivity of nanomaterial-based biosensors have led to major advances in the development of new methodologies for early detection. Due to its submicron dimensions, it allows simple and fast

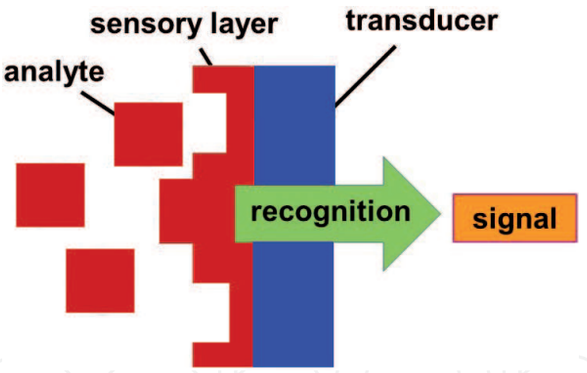


Figure 1.
Schematic presentation of a biosensor.

analysis in vivo. Their reactivity, toughness and other properties are also dependent on their unique shape, size and structure. In addition, the application of nanomaterials to biosensors provides different detection limits depending on the samples to be analyzed and facilitates the adjustment of the sensitivity level according to the needs.

2. Experimental

2.1 Synthesize of the novel nanomaterials

2.1.1 Graphdiyne

The synthesis of the GDY was reported in the literature as follows:

Graphdiyne (GDY) was prepared on the copper surface by a cross-linking reaction using hexaetynylbenzene (HEB) as a monomer. Firstly, hexakis [(trimethylsilyl) ethynyl] benzene (HEB-TMS) was prepared using Negishi cross-linking reaction. Then HEB monomer was obtained by the addition of tetrabutylammonium fluoride into tetrahydrofuran solution of HEB-TMS with stirring at 0°C for 10 minutes. Finally, GDY in the presence of pyridine was successfully grown on the surface of copper foils by a cross-coupling reaction of the HEB monomer for 72 hours at 60°C under a nitrogen atmosphere. After the reaction was completed, GDY grown on copper foils was removed by ultrasonic treatment and concentrated by rotary evaporator, and then washed with heated acetone and N,N-dimethylformamide. The GDY powder was refluxed with dilute hydrochloric acid and sodium hydroxide, respectively at 80°C for 3 hours. It was then washed repeatedly and centrifuged. Finally, black GDY powder was obtained by centrifugation and drying vacuum [8].

2.1.2 Gold nanostructures

According to the modified El-Sayed method the synthesis of the gold nanorods (GNRs) was performed as follows:

Ttwo solutions were prepared as seed solution and growth solution. For the seed solution, ice-cold sodium borohydride ($NaBH_4$) (0.3 mL, 0.01 M) was added to the solution mixture containing hydrogen tetrachloroaurate ($HAuCl_4$) (0.5 mM) and cetyltrimethylammonium bromide (CTAB) (0.2 M) in a volume ratio of 1:1, and the entire reaction mixture was incubated at room temperature for 3 hours. For the growth solution, a 200 mL solution containing $HAuCl_4$ (0.5 mM) and CTAB (0.1 M) was made and 6 mL of silver nitrate ($AgNO_3$) (4 mM) was added to it. Following this, 0.5 M sulfuric acid (H_2SO_4) (1 mL) and 0.0788 M ascorbic acid (1.4 mL) were

added and mixed gently. In the last step, the seed solution (0.24 mL) was added to the growth solution mixture and left at room temperature for a period of 12 hours. The brownish colored solution was centrifuged at 9000 rpm (2 times) for 30 minutes to remove unbound CTAB and stored at room temperature (28°C) [9].

2.1.3 Inorganic nanomaterials

The synthesis of Zirconium Phosphate Nanoparticle (ZrP-NP) is described in this section as one of the inorganic nanomaterials.

Zirconium Phosphate (ZrP), one of the inorganic nanomaterials, has been synthesized by hydrothermal process. First, 1.6 g of $ZrOCl_2.8H_2O$ was added to 30 mL of DI water and stirred continuously. Then 15 M H_3PO_4 (10 mL) was added to this prepared solution and stirred continuously for 30 minutes. The solution was transferred to a hydrothermal autoclave (50 mL) and heated in an air oven at 200°C for 24 hours. The products obtained were collected by centrifugation and washed several times with ethanol and deionized water. In the last step, the purified ZrP powder was dried in an air oven at 50°C [10].

2.1.4 Nanozymes

The synthesis of the core-shell Au@Co-Fe hybrid nanoparticles is described as peroxidase mimetic nanozyme.

In the synthesis of the core-shell Au@Co-Fe hybrid nanoparticles as the peroxidase mimetic nanozyme, gold nanoparticles (AuNPs) with the average diameter of 22 nm were synthesized by citrate reduction of $HAuCl_4$. Briefly, 1.5 mL of 1% (w/v) sodium citrate solution was added to 21 mL of 0.8 mM $HAuCl_4.3H_2O$ solution at boiling point while the solution was stirred vigorously. After hanging its color from pale yellow to deep red, the mixture was stirred for 15 min and let to cool to room temperature and, then stored at 4°C until use. In the second step, 1 μL tween 20 was added to 1.5 mL of the synthesized AuNPs. Then, 100 μL of $FeSO_4$ 0.18 M and 180 μL of $CoCl_2$ 0.1 M were added to the mixture, and incubated at the room temperature for 24 h. After that, the mixture was centrifuged and washed with deionized water [11].

2.1.5 Hybrid nanocomposites

One of the hybrid nanocomposites is reduced graphene oxide-magnetite nanoparticle (RGO-Fe_3O_4 NP) and its synthesis is described below according to the literature [12].

Reduce graphene oxide magnetite nanoparticle (RGO-Fe_3O_4 NP) hybrid was synthesized by alkaline reduction. For this purpose, the powder was redispersed in the 0.5 mg mL^{-1} graphene oxide (GO) suspension. Citric and ascorbic acids were added and the mixture was stirred at 55°C (12 hours). 1 M NaOH was added and the mixture It was stirred again at 95°C (6 hours). After centrifugation at 10000 rpm (RCF = 1118 x g), the solid is filtered, washed, and dried in vacuum during 24 hours [12].

2.1.6 DNA nanomaterials

Y-DNA was prepared by mixing equimolar amounts of three single stranded DNA (ssDNA), two long and one short. The two long sequences have regions that hybridize to the shorter one. One of the fields is not completely linked to the corresponding fragment. Thus, the target miRNA became able to replace this fragment

and remove the Y-DNA nanostructure. ssDNAs were dissolved in hybridization buffer at 10 μM final concentration per sequence and annealed to form the desired Y-shaped DNA: annealed at 95°C for 2 minutes, cooled to 65°C and incubated for 5 minutes, followed by 2 minutes while its temperature dropped to 60°C and cooled to 20°C at a rate of 1° per minute. The final products were stored at 4°C. Double stranded substrates were formed by mixing in the hybridization buffer. The mixture was heated to 95°C for 5 minutes and slowly cooled to 4°C, then allowed to stand at room temperature for 20 minutes to form a specific double stranded substrate [13].

2.1.7 DNAzyme

DNA phosphorylation was made by incubating 200 pmol of FS1 with 20 units of T4 polynucleotide kinase (PNK) at 37°C for 30 min in a 100 μL reaction mixture containing 50 mM Tris–HCl (pH 7.6 at 25°C), 10 mM $MgCl_2$, 5 mM 1,4-Dithiothreitol (DTT), 0.1 mM spermidine and 1 mM adenosine 5′-triphosphate (ATP). The reaction was stopped by heating the mixture at 90° C for 5 minutes. RFT1 (100 μM) and 2 μL RFS1 (100 μM) were then added to the solution, and the mixture was heated to 90°C for 40 seconds and cooled to room temperature for 10 minutes. In the last step, 10 units of T4 DNA ligase were added for DNA ligation at 25°C for 2 hours. The ligation mix contains 10 mM $MgCl_2$, (150 μL) 40 mM Tris–HCl (pH 7.6 at 25°C), 10 mM DTT and 0.5 mM ATP. The products were concentrated by standard ethanol precipitation and further purified by polyacrylamide gel electrophoresis [14].

2.1.8 Carbon Nanodots

The syntheses of carbon nanodots (CDs) will describe according to the literature [15].

CDs were synthesized hydrothermally with citric acid and ethylenediamine (EDA). Initially citric acid (3.0 g) and ethylenediamine (1875 μL) were dissolved in 30 mL of distilled water. The solution was then transferred to a 500 mL round bottom flask and heated at 150°C for 5 hours. The product was dialyzed against ddH_2O to obtain CDs. CDs powder was obtained by evaporating, redispersed in deionized water, and stored at 4°C for later use [15].

2.1.9 Carbon black nanomaterials

Carbon black (CB) is produced by the reaction of a hydrocarbon fuel such as gas or oil with a limited supply of combustion air at temperatures of 1320 to 1540°C. The hydrocarbons which were degraded from polyethylene (PE) or high density polyethylene (HDPE) at the pyrolysis step were injected into decomposing chamber. They were introduced to pass through dc-plasma jet, and were decomposed into the carbon particles. The carbon particles were cooled down in the stream of nitrogen and they were deposited on the surface of outer graphite chamber after decomposition by the plasma jet. As-synthesized carbon black samples were characterized by the analytical instrument without further purification in the case of carbon black synthesis. Two major processes are the oil furnace process and the thermal process. The oil furnace process accounts for about 90 percent of production, and the thermal, about 10 percent. Two other processes are, the lamp for production of lamp black and the cracking of acetylene to produce acetylene black. However, these are small-volume specialty black operations that constitute less than 1 percent of total production in this country [16].

2.1.10 Nanodiamonds

For the nanodiamond synthesis the graphitic C_3N_4 (g-C_3N_4) used for the starting material which prepared by a benzenethermal reaction between $C_3N_3Cl_3$ and $NaNH_2$ at 220°C for 12 hours. For the synthesis of the C_3N_4, 1.10 g (6.0 mmol) $C_3N_3Cl_3$(1,3,5-trichlorotriazine) and 0.70 g (18.0 mmol) $NaNH_2$ (sodium amide) powders were put into a 50 mL teflon-lined autoclave, which was then filled with benzene up to 90% of the total volume. The autoclave was sealed and maintained at 180–220°C for 8–12 h, then allowed to cool to room temperature naturally. The mixed product was washed three times with distilled water, acetone and again distilled water to remove NaCl impurities, some organic-like impurities. The g-C_3N_4 obtained in such a way is a light yellowish brown powder of amorphous-like, poorly crystalline particles [8]. The resulting yellow powders was dried in vacuum at 50°C for several hours. The sample was compressed to a desired pressure at room temperature, heated to 800–2000°C for 5–30 min, and then quenched and decompressed to ambient condition [17].

2.1.11 Magnetic nanoparticles

Magnetic nanoparticles (MNP) were prepared by chemical co-precipitation and then processed under hydrothermal conditions. Briefly, iron (II) chloride and iron (III) chloride (1:2) were chemically precipitated at room temperature (25°C) by adding 30% ammonium hydroxide at pH=10.0–10.4. The precipitates were heated at 80°C for 35 minutes with continuous stirring and washed in deionized water and ethanol [18].

3. Result and discussion

3.1 Graphdiyne

Graphdiyne (GDY) is a new two-dimensional all-carbon allotrope composed of benzene rings and alkyne unites.

The carbon based nanomaterials are usually used to build electrochemical biosensors because of their physical and chemical properties. According to conventional carbon nanomaterials, GDY possesses richer carbon chemical bonds, which are of great importance for their practical applications. More importantly, GDY has a typical 2D structure similar to graphene, but also has the properties of three-dimensional materials such as a hard carbon network and uniformly distributed pores that can greatly increase active bonding areas [19, 20].

Figure 2 illustrates surface characterization of GDY [21].

As can be seen from this figure it is clear that GDY has a porous structure which is very important in sensor design to the effective diffusion of the analyte to the sensor surface.

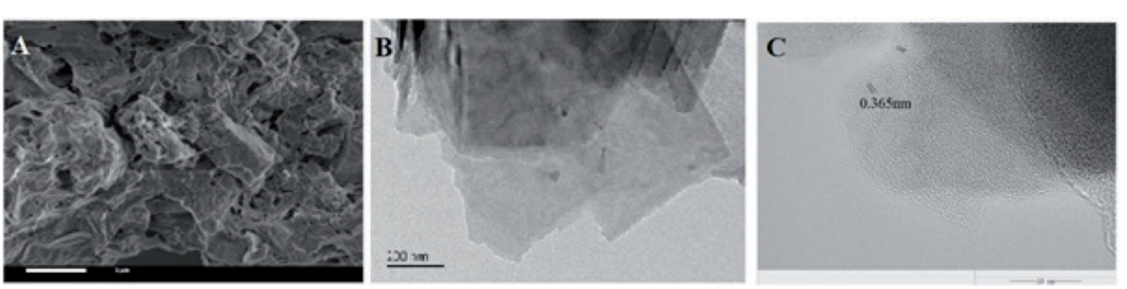


Figure 2.
A) SEM, B) TEM and C) HRTEM of GDY.

There are studies in which GDY has been used in the preparation of electrochemical enzyme biosensors [21], for microRNA testing [22] and in the determination of bacterium [23]. GDY was investigated as matrix for tyrosinase (a model enzyme) immobilization to create a mediator-free GDY based biosensor for rapid detection of bisphenol A (BPA). In this study between different carbon nanomaterial based biosensors including carbon nanotube and graphene was compared and it was reported, GDY-based tyrosinase biosensor performed better analytical for BPA detection than CNTs and graphene-based biosensors [21]. A new photoactive material has been synthesized that integrates the properties of MoS_2 and GDY to implement ultra-sensitive detection of microRNA [22]. Controllable synthesis of two-dimensional graphite nanosheet (GDY NS) is of great importance for the clinical diagnosis and treatment of tuberculosis [23].

It is though that as a new promising 2D all-carbon nanomaterial after graphene, graphdiyne with intriguing properties would inevitably attract the general interest of scientists.

3.2 Gold nanostructures

Metal nanoparticles (NPs) such as gold and silver NPs have gained immense recognition in nanosensing and diagnostic applications [24, 25]. Therefore, ease of synthesis, versatile surface functionalization and long term stability of gold nanomaterials increases their potential as efficient detection probes [26].

Gold nanostars modified with biotin were used for streptavidin determination [27]. Sensing applications using other shapes of gold nanomaterials include the use of gold nanowires and nanocubes for detection of bacteria in human kidney infection and catechol, respectively [28, 29].

Gold nanorods have also employed as a SERS substrate where in they have achieved highly sensitive and selective detection of DNA [30].

It has been reported that the nanosensor based on gold nanorodes is highly reproducible and has excellent selectivity. It was also reported the nanosensing platform is reliable, facile, cost-effective and less labor intensive. The nanomaterial with aspect ratio tunable property can be possibly used for several biomedical applications.

Figure 3 illusrates TEM and SEM images of some kind of gold nanosructures [27–30].

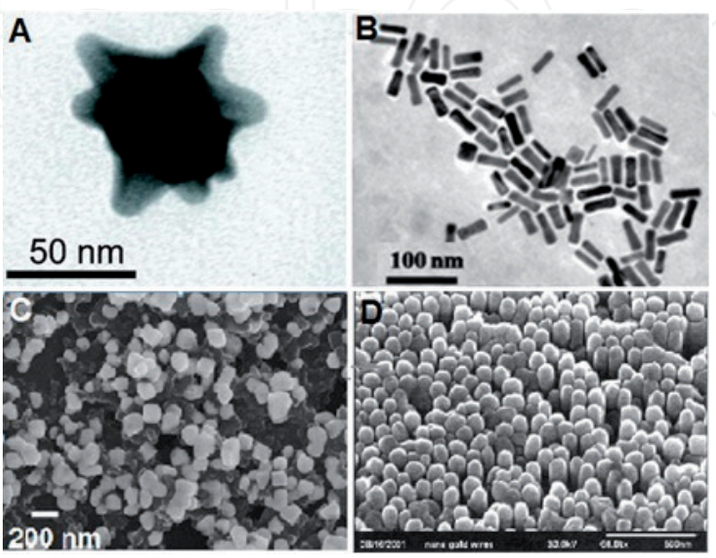


Figure 3.
TEM (A,B) and SEM (C,D) images of gold nanostar (A) [27], gold nanorods (B) [28], gold nanoparticle (C) [29] and gold nanowire (D) [30].

3.3 Inorganic novel nanomaterials

Recently, inorganic nanostructured materials have gained widespread attention as potential electrode materials of electrochemical sensors with excellent structural adjustability and other properties [31, 32].

In the past few years, binary metal oxides (denoted BMOs) are considered as one of the state-of-the-art electrocatalyst materials for various electrochemical applications [33, 34]. Among the different categories of BMOs, transition-metal phosphates/phosphides (denoted TMPs) have attracted increasing attention as a promising electrocatalyst [35–37]. Ultrathin cobalt phosphate-based modified electrode was used for the non enzymatic electrochemical determination of glucose [38]. α-zirconium phosphate (α-ZrP) based electrocatalysts have been recognized as crucial for numerous electrochemical applications [39]. The sensitive electrochemical sensing probe using the ZrP nanoplates was successfully applied for Furazolidone detection [10].

Figure 4 illustrates surface characterization of ZrP [10].

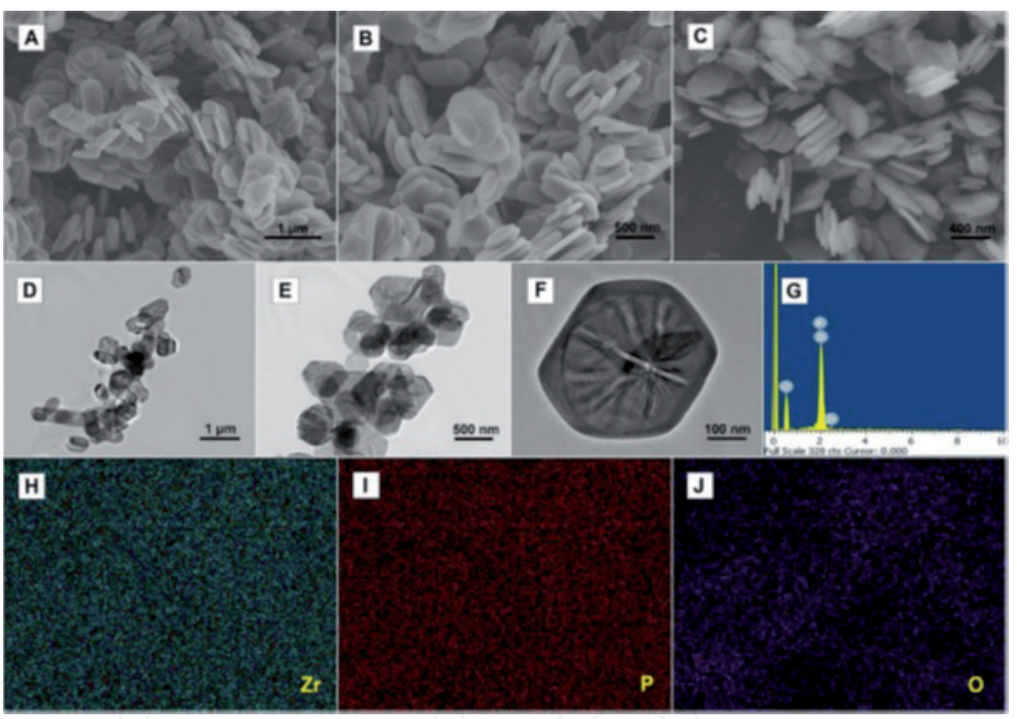


Figure 4.
(A–C) FEG-SEM image, (D–F) TEM images, (G) EDX spectrum, and (H–J) elemental mapping of ZrP.

3.4 Nanozymes

In the last decade, artificial nanomaterials, which exhibit properties similar to enzymes, have been shown as highly stable and low-cost alternatives to enzymes in electrochemical biosensing.

Nanozymes, combining the advantages of chemical catalysts and enzymes [40, 41], outperform natural enzymes because they are usually synthetized using low-cost, simple, and mass-production methods and offer high operational stability and self-life, robust catalytic performance [42–45]. Moreover, the smooth surface modification of nanomaterials provides more room for modifications than the natural enzymes. In addition, their inherent nanomaterial properties impart them both tunable and tenable catalytic activity [46, 47].

Figure 5 illustrates the schematic presentation of the enzyme-based and nanozyme-based immunoassay.

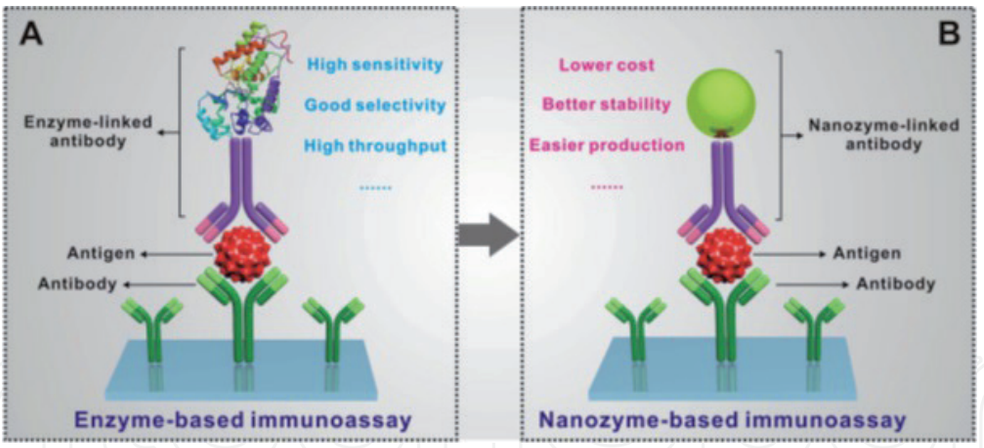


Figure 5.
Comparison of (A) natural enzyme-based immunoassays and (B) nanozyme-based immunoassays [46].

The lack of selectivity of nanozymes is compensated for by using specific bioreceptors. However, it is important to be aware of the current lack of bio-ligands for emerging analytes and that their use compromises both stability and the low cost of nanozymes [48].

Affinity ligand-based electrochemical biosensors using nanozymes have been successfully developed and exhibit some excellent merits such as higher selectivity and sensitivity, lower cost, shorter detection time, and better signal readout [49].

Nanozymes, being a special type of nanomaterial, can be exploited in electrochemical affinity biosensing as electrode modifiers, nanocarriers, and/or catalytic labels. These multi functional nanozymes, which include PtNPs/CoTPP/rGO [49], Pd/APTES-MCeO$_2$-GS [50], rGO-NR-Au@Pt [51], Mn_3O_4 and Pd@Pt nanoflowers [52], Fe_3O_4/PDDA/Au@Pt [53], MWCNTs/ GQDs [54, 55], and FeS_2-AuNPs [56], have been decorated with detector antibody (Ab_2) [49, 50], detector antibody (Ab_2) + HRP [51, 54, 55], AuNPs + Ab_2 [56], detector aptamer (Apt_2) + HRP [47], or (Apt_2) + HRP + G-quadruplex/hemin DNAzyme [46]. It is important to note that these nanozymes are often dressed with the natural enzyme to further enhance the sensitivity [51, 54, 55].

The combination of nanozyme-based electrochemical affinity biosensors with personalized equipment such as smartphones and/or portable low-cost devices will also be exciting to move forward in point-of-care testing. This nanozymes development to achieve catalytic activity and efficiency comparable or even better than natural enzymes will bring a revolution to conventional electrochemical biosensing and more practical applications in other expectation fields.

3.5 Hybrid nanocomposites

Hybrid sensing materials, which are organized by interaction of organic molecules onto inorganic supports, have been developed as a novel and hopeful class of hybrid sensing probes. Magnetic silica hybrid rather than other hybrid materials such as polymer, titania, and selfassembled monolayers [57–60] provides low toxicity, simple separation via external magnetic field, stability, biocompatibility and thermally stable advantages [61–63].

Biosensors prepared using hybrid materials were used to detect biological materials by thermal, electrical or optical signals. Examples of various applications of biosensors can be mentioned as environmental monitoring [64], forensic science [65–67], water characteristic testing [68], defense and the military [69], biomedicine, food industry and medical diagnosis [70].

Magnetic silica hybrids were reported as fluorescent, colorimetric, electrochemical and Surface-enhanced raman spectroscopy (SERS) sensing probes [71]. Inorganic mesoporous material is one of the best materials as molecular catalysts due to its thermal stability, easy production and modification. It used in the fields of biomedicine, electronics, and physicochemistry. Silica-coated Fe_3O_4 nanoparticle (Fe_3O_4@SiO_2 NPs), have good excellent conductivity, electrochemical transducers, biocompatibility, catalytic activity, separation ability and low toxicity properties to produce "electronic wires" to increase the electron transfer between redox centers and electrode surfaces in proteins [72].

Figure 6 illustrates the surface characterization of Fe_3O_4@ SiO_2 nanoparticles performed by transmission electron microscopy (TEM) [57].

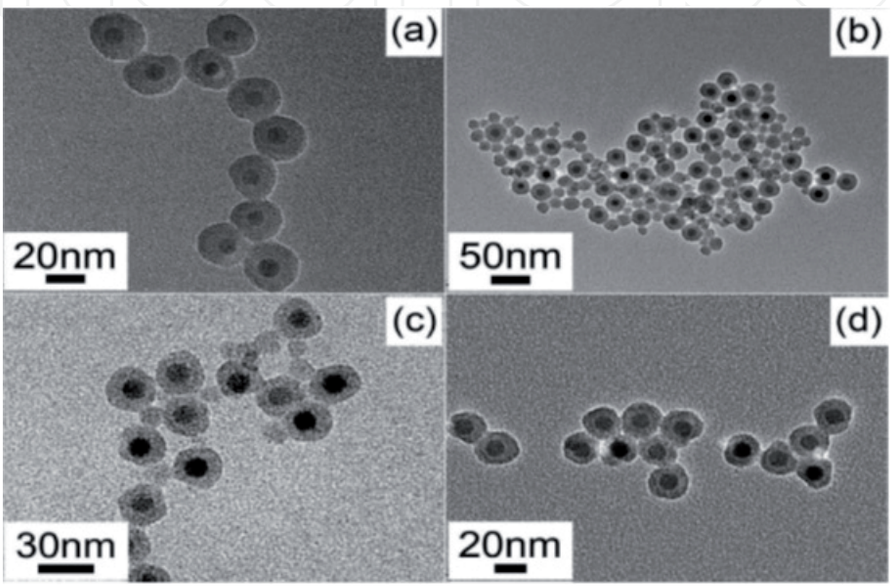


Figure 6.
TEM images of Fe_3O_4@ SiO_2 NPs with Fe_3O_4 sizes of (a) 8.8 nm and (b–d) 12.2 nm.

3.6 DNA nanomaterials

DNA nanomaterials have been widely used in bioassays due to their promising properties for sensitive and specific detection of biomolecules. The electrochemical biosensor has received greater attention in clinical diagnosis due to its high sensitivity, easy controllability and low cost [72]. For this reason, the biomolecular recognition and signal amplification based on electrochemical platform to achieve miRNAs detection still need to be considered.

In recent years, legion nucleic acid nanostructures have been applied to biological detection, including DNA tetrahedron, DNA gels, DNA dendrimers, and so on [73–75]. Y-shaped DNA (Y-DNA), as a constant nanostructure with high selectivity, provides an effective method for completely measuring target molecules [76]. Y-DNA consists of three oligonucleotides that are partially hybridized to each other. Some older biosensors used this feature to perform DNA detections where one DNA stand is fixed to the surface, another DNA stand and target DNA are added to form a specific structure [77].

Numbers of signal amplification strategies have been developed, including hybridization chain reaction (HCR), strand displacement amplification (SDA), catalytic hairpin assembly (CHA) and rolling circle amplification (RCA) [78–81]. The HCR consists of a trigger sequence and two partially complementary hairpin probes. Once triggered, the two hairpin probes can autonomously hybridize continuously [82].

Compared to HCR, this reaction consists of more complex components, including a trigger sequence, two double stranded substrates with bridging loops in the middle, and two helper sequences [83]. Thus, non-linear HCR can achieve higher rates of amplification and molecular weights [84].

To join non-linear HCR and Y-DNA nanostructures, the Y-DNA's terminals were designed as triggers that could initiate the amplification reaction. As a result, the new biosensing method can provide high-precision and selective detection of biological molecules. An unlabeled DNA nanostructured electrochemical biosensor was designed to detect miRNA-25, which is reported to be a potential molecular biomarker for non-small cell lung cancer and heart failure [85, 86].

Expanding the application of DNA nanomaterials to bioassays in the future may enable early and effective detection of various diseases.

3.7 DNAzyme

DNAzymes are single-stranded (ss) DNA sequences are able to catalyze a number of reactions, including cleavage of the phosphodiester backbone at a ribonucleotide or deoxyribonucleotide site [87]. It has been shown that metal ions play an important role in the catalytic process and are essential for the catalytic activity of most known DNAzymes [88].

The ability to select a DNAzyme with metal ion specific activity without previous chemical knowledge of the DNAzyme structure, and then to subsequently modify DNAzyme binding arms and other insignificant nucleotides with minimal to no effect on sensitivity and selectivity has made DNAzymes ideal metal-selective components for new metal ion sensing technologies. RNA-cleaving DNAzyme is a very useful biomaterial for the determination of metal ions, but some parts of DNAzymes can be cleaved by several metal ions, which makes different concentrations of metal ions difficult to distinguish [89].

In the last two decades, the rapid development of nanomaterials and biomaterials [90] offers more opportunities to improve electrochemical sensor performance. For the determination of Cu (II) and Hg (II), many highly sensitive sensors are manufactured using small molecules, peptides, proteins and antibodies at low cost.

The ligand sites of proteases composed of nitrogen, oxygen or sulfur can combine with heavy metal ions to form a stable complex [91]. Cu(II) is a small ion that has to be chelated first and then bind to the antibody recognition [92]. Both antibody and enzyme work best under physiological conditions that limit application in real environment. DNA is not only the genetic material of most living organisms, but also an excellent biological functional material [93].

Metal ions can be specifically bound with a single-stranded DNA to form a stable metal-mediated DNA, and this mechanism is applied to detect metal ions [94, 95]. Therefore, numerous studies have focused on the newly discovered biosensor using different DNA-based aptamers functionalized with nanomaterials to increase sensitivity. DNAzymes that break down RNA as DNA-based catalysts are obtained through in vitro selection, which turned out to be a very useful platform for the identification of metal ions. After binding with heavy metal ions, many biochemical and biophysical studies have been conducted on DNAzymes due to their high metal ion selectivity and high catalytic efficiency [96]. Therefore, DNAzymes have been applied in various biosensors (colorimetric, electrochemical and fluorescent) that realize the detection of various metal ions such as Mg(II) [97], Ag(I) [98], Pb(II) [99], Zn(II) [100], Hg(II) [101], UO_2(II) [102].

The field of DNAzyme-based metal ion sensing is continuing to develop for future cellular and portable detection technologies.

3.8 Carbon nanodots

Carbon dots (CDs) are nanomaterials less than 10 nm in size and became the new potential material for the electrode modifier [103]. Formerly, CDs have been applied in electrochemical sensing platforms, mainly focusing on their electrocatalytic properties toward analytes of interest [104, 105] rather than electrode modifiers. Thus, the studies on carbon dots owing a noticeable potential to be used as electrode modifiers in electrochemical techniques to increase the sensitivity of the electrochemical sensor has been exploited.

Recently, a new member of CDs, have gained attention because of their water solubility, fine properties, high luminescence, low cytotoxicity and good conductivity [106]. Depending on the precursors employed in their synthesis, CNDs are surrounded by different functional groups including, among others, hydroxyl, amide groups and carboxyl which facilitate the immobilization of biomolecules. Hence, due to their ability to be modified with a wide variety of biomolecules, and in conjunction with the excellent properties mentioned above, CNDs have been employed in many biological applications such as solar cell development and photocatalysis [107, 108]. Concerning the employment of CNDs for electrochemical biosensors, it should be highlighted that despite the previously mentioned advantages, very few attempts to incorporate CNDs into electrodes are reported. Reporting the application of CNDs in electrochemical sensors are focused on the electrocatalytic properties of this nanomaterial toward oxygen reduction [109], biomedical application [110], exploited for glucose biosensing [111] and DNA sensing [112].

Transmission electron microscopy (TEM) of carbon nanodots in different scale from 20 nm to 2 nm are illustrate in **Figure 7** [110].

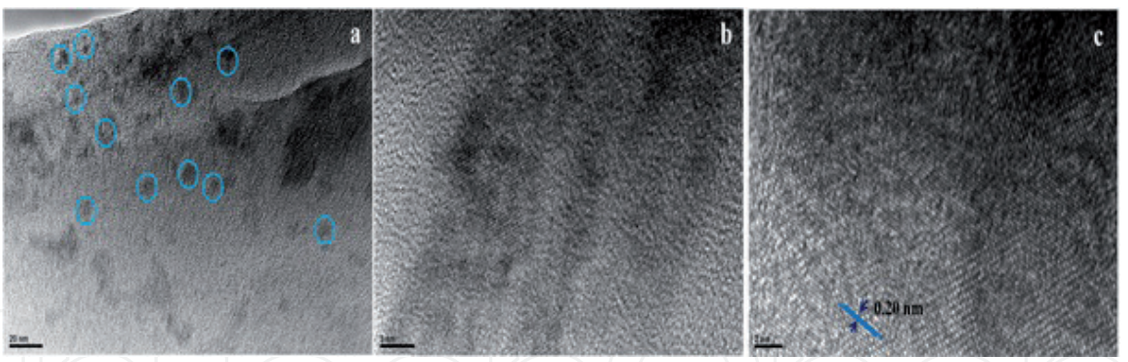


Figure 7.
High resolution transmission electron microscopic images of fish scale derived carbon nanodots (a-c).

3.9 Carbon black nanomaterials

Since the discovery of carbon nanotubes, carbon-based nanomaterials being researched in various disciplines including electrochemistry. An old and cost-effective material recently called carbon black (CB) reinvented. CB has good electrical conductivity, dispersible in solvents, possibility of easy functionalization and has a large number of defect areas and fast electron transfer kinetics [113–116].

Previously, CB's main application in the electrochemical field was based on the design of sensors for analyte detection in fuel cell and gas phases for lithium and sodium batteries [117, 118]. However, until 2009, only a few CB-based electrochemical sensors were reported for analyte detection.

Among nanomaterials, CB demonstrated high potential in customizing all from the oldest carbon paste to glassy carbon and printed electrodes thanks to their fascinating electrochemical properties combined with cost effectiveness.

One of the main properties of CB is its ability to produce easily stable dispersions in a variety of solvents such as ethanol, acetonitrile, a mixture of dimethylformamide water [119], chitosan [120], or di hexadecylphosphate water solution [121], usually at a concentration of 1 mg/mL.

CB is widely used in the design of biosensors with a variety of biological recognition elements including enzymes, DNA and antibodies. The main potential of the enzyme combination with CB is based on the outstanding advantages this nanomaterial has in enhancing the biosensor sensitivity. CB can increase both conductivity and enzyme loading areas, thus causing increased signals and hence higher sensitivity. Some examples have shown that CB is a compatible substrate for the immobilization of enzymes in the design of amperometric biosensors [122].

Immunosensors have attracted great attention for specific, sensitive, cost-effective and in-field analysis. Examples of CB-based immunosensors in unlabeled configuration have been reported in the literature [123, 124].

Alongside traditional bioreceptors such as enzymes, antibodies, and nucleic acids, CB also demonstrated the ability to improve their analytical performance by combining with alternative biological recognition elements or molecularly imprinted polymers [125].

Besides the biosensor application, CB was used in sensor design for both single analyte detection and multiple analysis, showing increased sensitivity thanks to its high conductivity, number of defective areas and surface area. Nowadays, most CB-based detection systems are mainly sensors, but in recent years there has been a sharp increase in publications in the development of enzymatic, immuno, and DNA biosensors [126].

CB is a new generation material due to its environmentally friendly properties in terms of costs and environmental impact.

The morphological properties of the synthesized carbon black by using commercial and waste polystyrene (PS) and high density polyethylene in different pyrolysis conditions were illustrated in **Figure 8** [16].

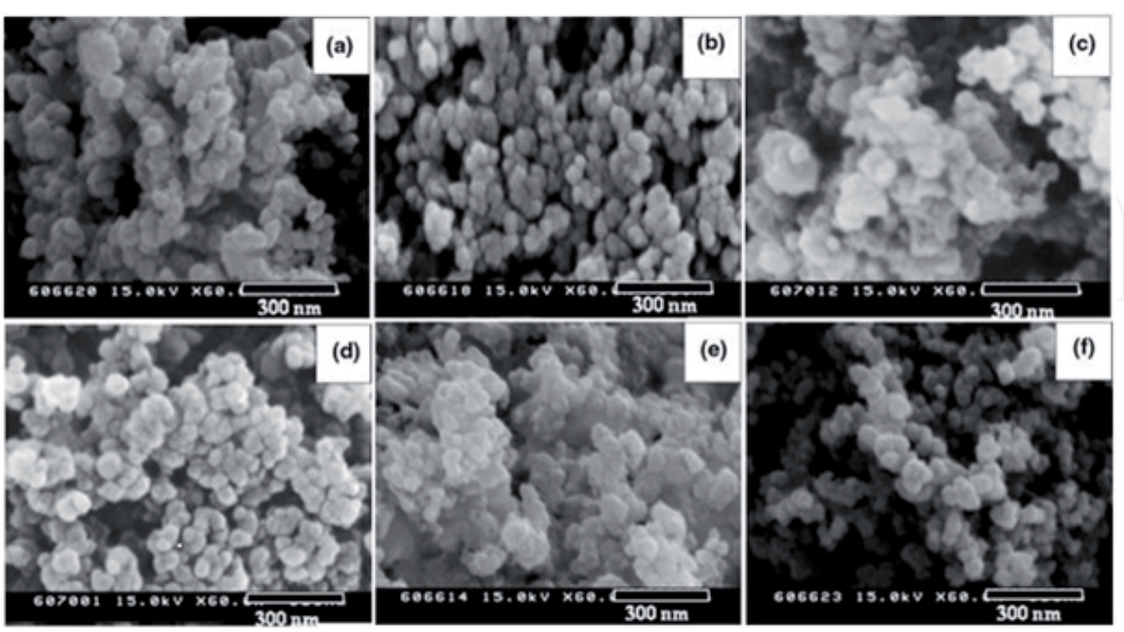


Figure 8.
FE-SEM images of the carbon black obtained from: A commercial PS pyrolyzed at 500°C; b commercial PS pyrolyzed at 900°C; c waste PS pyrolyzed at 500°C; d waste PS pyrolyzed at 900°C; e high density polyethylene (HDPE) pyrolyzed at 500°C; f HDPE pyrolyzed at 900°C.

3.10 Nanodiamonds

Nanodiamonds (ND), a new member of the carbon nanoparticle class, has recently received much attention in drug delivery, bio-imaging, and biosensor applications due to its physical and chemical properties [127].

Nanodiamond (ND) is of great interest in various fields of material science due to its various functional groups. An electrochemical biosensor containing copper, nano-diamond (ND) and carbon nanotube (CNT) was built to detect the amino acids of Parkia Seeds (PS). Electrochemical reaction of PS was carried out with composite electrodes prepared using nanodiamond [128].

The AFM and SEM characterization of nanocrystalline diamond (NCD) and boron doped nanocrystalline diamond (BDND) were illustrated in **Figure 9** respectively [129, 130].

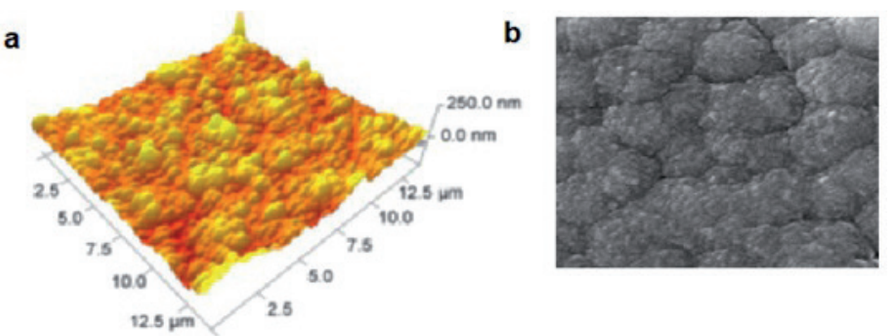


Figure 9.
(a) AFM topographic images of NCD films and (b) SEM image of BDND film grown on a Si substrate.

3.11 Magnetic nanoparticles

Nanomaterials provide high surface areas and a biocompatible environment for enzyme loading. In the last decade, research of magnetic particles has resulted in their use in a large number of nano-sensing devices, providing ease of separation in solution.

Various iron magnetic nanoparticles (MNPs) have proven to be an excellent nanomaterial for electrochemical biosensing applications due to their electroconductivity, biocompatibility and ease of synthesis properties. They make important contributions to the development of electrochemical nanobiosensors. Functionalized magnetic nanoparticles can be directed by the external magnetic field to site-specific drug delivery targets. Iron and iron oxide nanoparticles have been studied as signal amplification elements in biosensing [131]. Among these materials, magnetite (Fe_3O_4), a Fe^{2+} and Fe^{3+} complex oxide, is one of the most studied super paramagnetic nanoparticles. It has unique mesoscopic mechanical and physical properties and has many potential applications in various fields such as cell separation [132] and microwave absorption [133]. Fe_3O_4 nanoparticles have been widely used for in vivo examination [134]. The direct binding of cholesterol oxidase to Fe_3O_4 magnetic nanoparticles was investigated and the kinetic behavior, stability and activity of bound cholesterol were investigated [135]. Due to its easy preparation process, low toxicity, strong superparamagnetism and good biocompatibility, Fe_3O_4 has recently been used in biosensors for glucose, ethanol and acetaminophen. Prepared biosensors showed fast response and high sensitivity with a wide linear range [136, 137]. Fe_3O_4 - Au nanoparticles, have been

successfully used for the first time in the dual-mode detection of carcinoembryonics antigens (CEA) and have correctly confirmed the presence of antigens [138].

Figure 10 illustrates TEM images of Fe_3O_4, Au and Fe_3O_4-Au nanoparticles [138].

Table 1 illustrates the studies based novel nanomaterials.

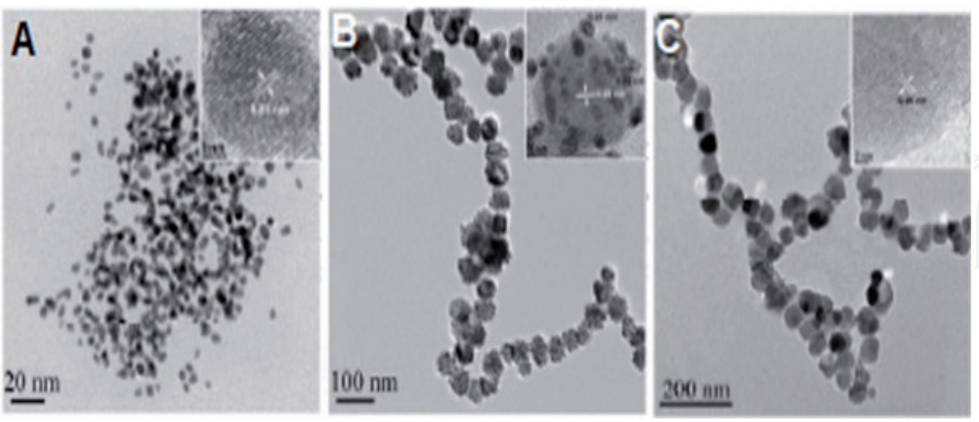


Figure 10.
TEM images of (A) Fe_3O_4, (B) Au and (C) Fe_3O_4–Au nanoparticles; the corresponding HRTEM images are inserted.

Nanomaterial	Analyzed	Detection limit	Linear range	Method	Ref.
Graphdiyne	Bisphenol A	$1,0 \times 10^{-7}$-$3,5 \times 10^{-6}$ mol/L	24 nmol/L	CV[1]	[21]
Hybrid Nanocomposite	Metronidazole	0,001–2444 μM	0,8 nM	CV and EIS[2]	[34]
Inorganic nanomaterial	Furazolidone (FZD)	0,009–339 μM	1,2 nM	CV, EIS and Amperometry	[10]
Noble metal nanoparticles	Alpha fetoprotein (AFP	0,1 pg./mL to 50 ng/mL	0,033 pg./mL	CV	[50]
Bimetallic Pt-Au/multi-walled carbon nanotubes	Organophosphorous pesticides	50 to 500 nmol/L	29,7 nmol/L	CV, Amperometric i-t curve and EIS	[64]
Quantum dots	Dopamine	0,375–450 μM	100 nM	Electro-chemiluminescence	[66]
DNAzyme-functionalized single-walled carbon nanotubes	Cu(II) and Hg(II)	Cu(II) 0,01–10,000 nM Hg(II) 5–10,000 nM	Cu(II) 6,7 pM Hg(II) 3,43 nM	EIS	[89]
DNAzyme Functionalized Single-Walled Carbon Nanotube	Silver Ion	10 pM to 10^6 pM	5 pM	UV–Vis Spectrometry	[98]
Carbon nanodots	Gene mutation	0,001–20 μM.	0,16 nM	CV and DPV[3]	[112]
Carbon-coated nickel magnetic nanoparticles	Acetaminophen	$2,0 \times 10^{-6}$ to $2,3 \times 10^{-4}$ mol/L.	$6,0 \times 10^{-7}$ mol/L	DPV	[137]
Carbon black	Bisphenol A	0,03 μ M	0,1–0,9 μM 1–50 μM	SVW[4]	[139]

Nanomaterial	Analyzed	Detection limit	Linear range	Method	Ref.
3D DNA nanonet structure	MicroRNA	36,083 fM	10 fM-1 nM	CV, DPV and EIS	[140]
Carbon nanodot	17ß-Estradiol	$0,5 \times 10^{-12}$ M	$1,0 \times 10^{-7}$ - $1,0 \times 10^{-12}$ M	CV and EIS	[141]
Carbon black	Photosynthetic herbicide	0,1–5 mu M	1 nM	Amperometric measurement	[142]
Metal-polymer hybrid nanomaterial	Human papillomavirus	1–100 pg. mu/L	2,74 pg. mu/L	CV and EIS	[143]
Nanozymes (magnetic metal organik framework)	Hydrogen peroxide (H_2O_2)	5 mu M-120 mM	0,9 mu M	CV, EIS and Amperometry	[144]
Gold nanorod	Aflatoxin	0,25–10 ng/mL	0,11 ng/mL	SPR[5]	[145]
Nanodiamond	Urea	0,1–0,9 mg/mL	0,005 mg/mL	Direct current voltage	[146]
Carbon dots, chitosan, gold nanoparticles	Patulin	1×10^{-12} - 1×10^{-9} mol/L	$7,57 \times 10^{-13}$ mol/L	CV and DPV	[147]

1: Cyclic voltammetry, 2: Electrochemical impedance spectrometry, 3: Differential pulse voltammetry 4: Square wave voltammetry, 5: Surface plasmon resonance.

Table 1.
Biosensor applications based navel nanomaterials.

4. Conclusion

Nanomaterials offer significant advantages, especially in sensor technology, due to their large surface area. When biocompatible nanomaterials are used as biorecognition layers, it enables the design of highly sensitive biosensors. Many nanomaterials, which are widely used today, are now being replaced by novel nanomaterials due to their physical stability, easy synthesis, easy fabrication, and cheapness.

Nanomaterials became important components in bioanalytical devices since they clearly increase the performances in the sense of detection limits and sensitivity down to single molecules detection.

Over content of this chapter aims to evaluate developments in the fields of new nanomaterial-based biosensors. Their production and potential applications for the direct and reliable detection of bioanalytes are described. In addition, research interests for the production of nanomaterial-based biosensors were encouraged with examples.

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