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REVIEW ARTICLE

Nanomaterials in bioelectrochemical devices: on applications enhancing their positive effect

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Abstract

Electrochemical biosensors and biofuel cells are finding an ever-increasing practical application due to several advantages. Biosensors are miniature measuring devices, which can be used for on-the-spot analyses, with small assay times and sample volumes. Biofuel cells have dual benefits of environmental cleanup and electric energy generation. Application of nanomaterials in biosensor and biofuel-cell devices increases their functioning efficiency and expands spheres of use. This review discusses the potential of nanomaterials in improving the basic parameters of bioelectrochemical systems, including the sensitivity increase, detection lower-limit decrease, detection-range change, lifetime increase, substrate-specificity control. In most cases, the consideration of the role of nanomaterials links a certain type of nanomaterial with its effect on the bioelectrochemical device upon the whole. The review aims at assessing the effects of nanomaterials on particular analytical parameters of a biosensor/biofuel-cell bioelectrochemical device.

Keywords Nanomaterials · Electrochemical devices · Biosensor · Biofuel cell · Analytical parameters · Biocatalyst

Abbreviations

CNT	Carbon nanotube
MWCNT	Multiwalled carbon nanotube
NAD	Nicotinamide adenine dinucleotide
NADH	Reduced form of nicotinamide adenine dinucleotide

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Introduction

Practical application of any methods of analysis is associated with the possibility of their miniaturization, conducting analyses at the site of sampling, ease of analysis and economic benefits in the production and operation of devices. Electrochemical biosensors and biofuel cells based on enzymes and microorganisms have firmly occupied a niche among devices used for analysis (Gonzalez-Solino and Lorenzo 2018; Lima et al. 2018; Mishra et al. 2018).

An electrochemical-type biosensor is an analytical device in which biological materials immobilized on a signal converter detect an analyte and change their electrochemical characteristics in response to external effects (analyte, temperature, pH, light, stress, etc.). The general operating principle of microbial/enzymatic biosensors and fuel cells can be schematically represented as follows (Fig. 1).

Various kinds of biological material used in bioelectrochemical devices release electrons and protons as a result of substrate transformation (or under the action of other factors of the environment). The electrode serves as an external acceptor of electrons, as a result of which an electric potential that can be measured is generated in the system. Thus, an external impact is converted into a signal, which can be detected using various converters; herewith, the value of the signal would depend on the amount of assayed compound/

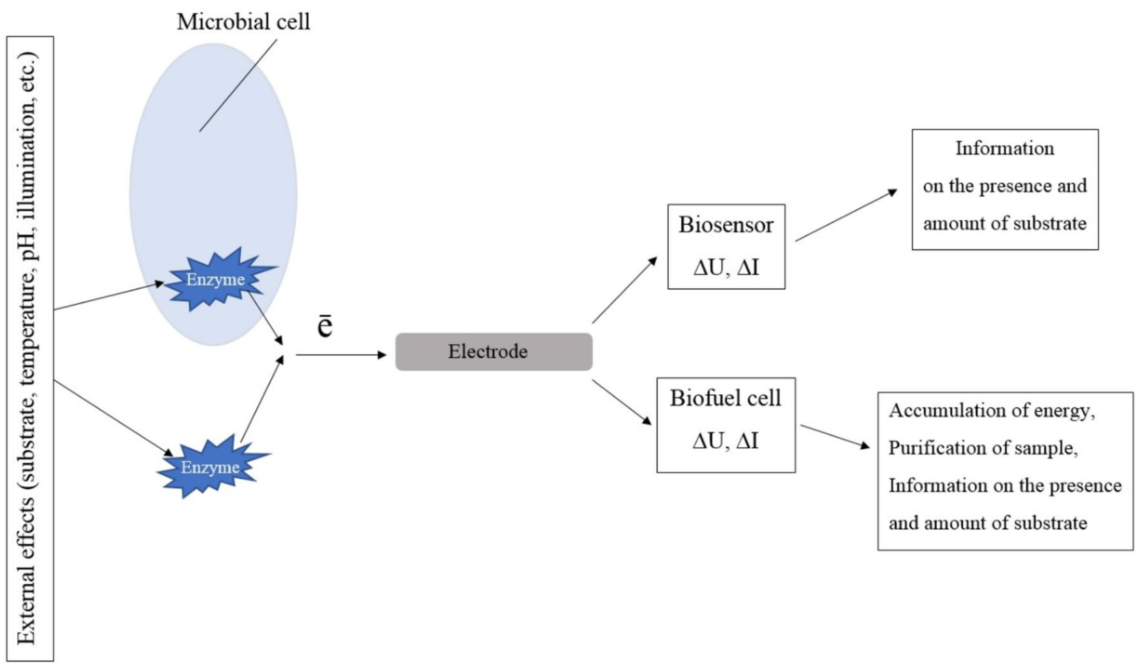

Fig. 1 Operating principle of electrochemical enzymatic/microbial biosensors and fuel cells

time and the external impact. Biofuel cells can be considered as an expansion of the diversity of electrochemical biosensor types, in which biological material converts the chemical energy of organic compounds or inorganic substances (fuel) into electrical energy. The connection of a load makes it possible not only to obtain an analytical tool (biosensor) but also to use the generated energy for other purposes. Biofuel cells require broad substrate specificity and (much) larger areas of their electrodes—anodes and cathodes—to increase their energy efficiency.

Establishing an electric contact between the biocatalyst and the electrode surface in bioelectrocatalytic systems—both in biosensors and fuel cells—is the main issue of their functioning.

Many biosensors developed to date have been successfully commercialized. For example, biosensors for assays of blood glucose in humans (Yoo and Lee 2010; Tarasov et al. 2021) and biological oxygen demand in effluents (Zulkifli et al. 2018; Do et al. 2019). The low stability and efficiency of biofuel cells limit their commercial use. At the same time, biofuel-cell devices are attractive because microorganisms that can be used as biocatalysts are widespread in the environment; the source of energy for them is organic substrate (both naturally occurring and human biowaste) present in water bodies or in soil biogeocenoses. Such devices are considered as a future alternative to traditional sources of energy (Ardakani and Badalians Gholikandi 2020; Arun et al 2020). Nevertheless, the main problems associated with immobilization and preservation of long-term activity of biomaterial, efficiency increase and stable operation of developed bioelectrochemical devices, are highly topical at present.

One of the materials that possess important properties and enable solving the associated problems are nanomaterials. These are objects in the range of 1–100 nm in size in at least one dimension (Miernicki et al. 2019; Sheikhzadeh et al. 2020). A dimensionality classification of nanomaterials, describing 36 classes of nanostructures, is given in the work of Pokropivny and Skorokhod (2008). Another work (Saleh 2020) considers the main classification of their types based not only on nanomaterial size but also on morphology, condition, and chemical composition. As applied to biosensors and biofuel cells, a classification by chemical composition is used: (1) inorganic nanomaterials consisting of (non) metal components; (2) carbon nanomaterials; (3) polymer nanomaterials (conjugated nanoparticles and coatings).

As the attitude to the use of nanomaterials is still associated with both their positive and, in some cases, negative effects, it is quite difficult to accept the final formula for their application, since the scope of their final use is unclear. In some cases, even a negative effect can be considered to obtain a final positive application. Thus, it can be summed up that the influence of nanomaterials on biological objects, their use in bioelectrochemical devices only expands knowledge about their properties and helps to develop strategies for their application, as well as to assess the possible risks of their use.

In this review, we consider particular analytical parameters, which can be changed by applying the most frequently used nanomaterials, and, by their example, demonstrate the biosensor and biofuel-cell characteristics that can be improved using them.

Production and modification of nanomaterials

The properties of nanomaterials depend on how they are produced, so the production methods should correspond to certain requirements. The main requirements are to provide the controlled composition of produced nanomaterials with reproducible properties and of definite sizes; the stability of produced nanomaterials; the high efficiency and cost effectiveness of the method used. It should be noted that there is no nanomaterial production method at present, which would have corresponded to all specified requirements. Two main directions are singled out in the production methods by the type of nanostructure formation: (1) the bottom-up approach, when nanoparticles grow or are assembled from separate atoms; (2) the top-down approach based on breaking particles to nanosizes (Mourdikoudis et al. 2018; Khan et al. 2019). Depending on the nature of nanomaterial synthesis, the production methods can be divided into chemical (electrolysis, reduction, oxidation, thermal decomposition, etc.), mechanical (pressure, compaction, cavitation processes, etc.), physical (evaporation, condensation, rapid heating/cooling, etc.) and biological (the use of microbes and biochemical processes) [Cele 2020; de Arnoldi Pellegrini et al. 2020; Jin et al. 2021; Parauha et al. 2021; Rai et al. 2021 (Fig. 2)].

Nanomaterial production techniques are constantly improved. Thus, carbon nanotubes (CNTs) were initially synthesized in gas phase processes at high temperatures [laser ablation (Radhakrishnan et al. 2006) and arc discharge (Qiu et al. 2004)]. Currently used methods are low-temperature thermal chemical vapour deposition (at less than 800 °C), which enables monitoring the parameters of produced nanomaterials—changing CNT length, diameter, orientation, purity, density, etc. (Singh et al. 2003; Di Pietrantonio et al. 2019). A number of studies (Griffiths et al. 2013; Hoang et al. 2018; Ding et al. 2019; Zhou et al. 2020; Makgabutlane et al. 2021) describe the techniques for producing carbon nanomaterials known to date, consider strengths and the weaknesses of each method, single out problems of commercial use and prospects for further industrial application. The replacement of expensive precursors by cheap raw materials, which would promote successful commercialization of the methods, is considered; also, attention is paid to ecological problems due to the formation of toxic wastes in CNT production (Griffiths et al. 2013).

It should be noted that CNTs can be produced by pyrolysis, with lignocellulose as initial raw material. This approach reduces production costs and enables using ecologically clean and renewable resources (Omoriyekomwan et al. 2020). Lignocellulose pyrolysis leads to the formation of high-molecular-weight polycyclic aromatic hydrocarbons, which serve as a carbon source for CNT synthesis (Sevilla and Fuertes 2010; Omoriyekomwan et al. 2019; Matamba et al. 2020). Traditional methods of metal nanoparticle production can be associated with the use of ionic liquids (Verma et al. 2019) and reduction of noble metal salts (Delbecq et al. 2019; Huggias et al. 2020). Methods of biological synthesis based on the ability of some microorganisms to synthesize various types

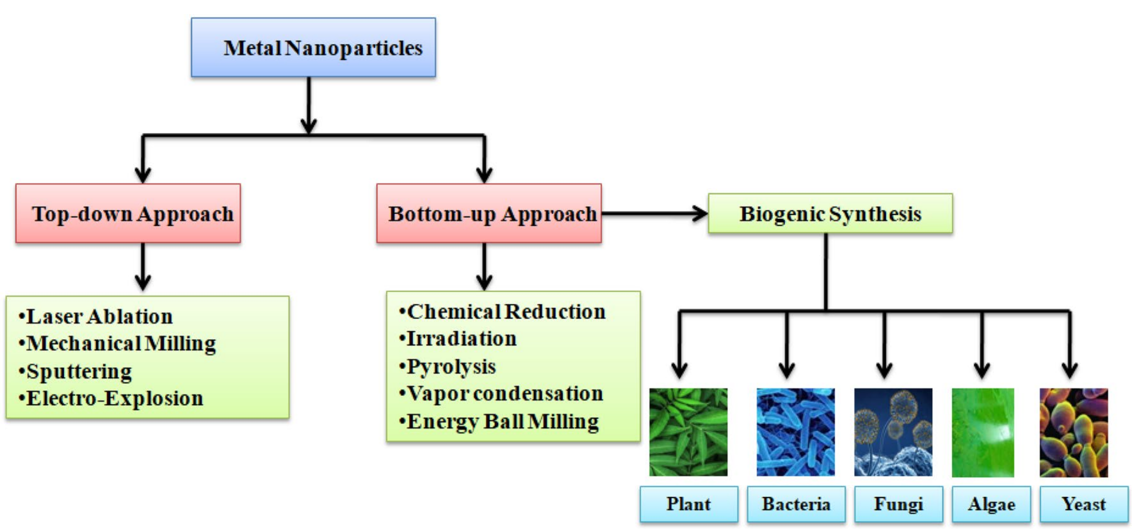

Fig. 2 Schematic representation of different synthetic methods. Reproduced from Rai et al., Nanomaterials 11:2901, Copyright 2021. Creative Commons Attribution 4.0 License. Published by Multidisciplinary Digital Publishing Institute

of nanoparticles from precursor materials have been of ever-increasing significance lately (Feng et al. 2018; Sadhasivam et al. 2020; Waris et al. 2021).

The synthesis process is completed, as a rule, by purification of synthesized nanoparticles. Thus, the medium containing a precursor material includes amorphous carbon, metal particles and other impurities depending on the production method. Purification of CNTs proceeds using thermal oxidation, high-temperature annealing, boiling, sonication and filtration (Capobianchi et al. 2007; Yu et al. 2020). Extraction and purification of metal nanoparticles produced by bacteria during extra- or intracellular synthesis have been studied insufficiently, which stimulates further research in this direction. Separation of intracellularly produced nanoparticles from the biomass requires additional stages of treatment, such as sonication or a reaction with suitable detergents, freeze-thawing, processes of heating and osmotic shock, enzymatic lysis of microbial cells containing intracellular nanoparticles, etc. (Iravani 2014).

Functions of nanomaterials in bioelectrochemical devices

The main function of nanomaterials is associated with the provision of effective electron transfer between biological material and an electrode in a biosensor or a biofuel cell. One of the main advantages of using nanomaterials in biosensors is the amplification of analytical signal and the increase of sensitivity; in some cases, the gain reaches several orders of magnitude. Nanoparticles may act as an "electron wire" between the enzyme active site and an electrode, contributing to an increase in the rate of direct electron-transfer turnover and decreasing the insulating action of protein. In particular, the use of gold or platinum nanoparticles for modification of electrodes creates a microenvironment similar to a natural system with redox proteins, which leads to a greater freedom of motion and orientation of protein with respect to the electrode (Solanki et al. 2011; Alarcon-Angeles et al. 2018). It should be noted that the effect of nanomaterials on particular parameters of biosensors and biofuel cells is not limited to only electron transfer; practically all characteristics of a bioelectrochemical device change at their participation. Here, we discuss the action of nanomaterials in greater detail.

Immobilization of biomaterial

One of the important parameters, which determine the efficient functioning of biosensors/biofuel cells as well as their application for the analysis of real objects, is associated with the immobilization of biomaterial in a bioelectrochemical device. Immobilization provides for the contact of biomaterial with a converter and the possibility of receiving a signal from biomaterial. The use of nanomaterials with high surface-area-to-volume ratios for immobilization of cells and enzymes leads to an increase of the electrode's effective area, and correspondingly, to an increase of the amount of biomaterial in an active state, which in turn affects the signal rise. The work of Ding et al. (2015) summarizes the main physico-chemical mechanisms of enzyme immobilization on nanoparticles leading to an increase in enzymatic activity (Fig. 3). If microbial cells are immobilized, the factors leading to a change in their activity when using nanomaterials

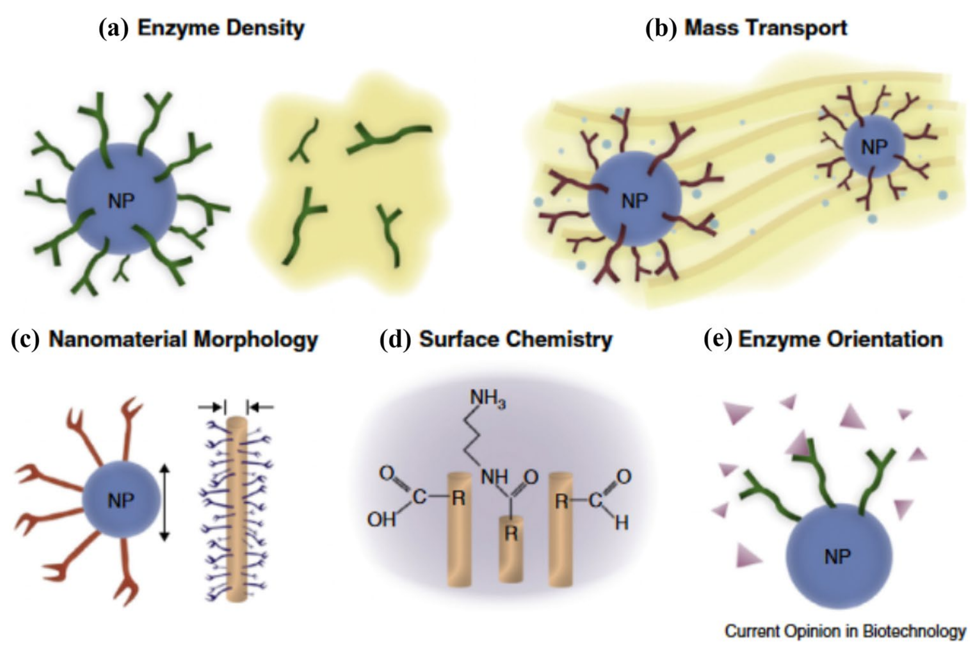

Fig. 3 Five mechanisms that are critical to enhanced enzymatic activity with enzymes immobilized onto NPs: **a** higher enzyme density and higher localized avidity, **b** enhanced mass transport, **c** increased surface curvature, **d** favourable surface functional group interactions and **e** favourable enzyme orientation for enzyme–substrate interactions, i.e. optimized enzyme–substrate trajectory. Reprinted from Ding et al., *Curr. Opin. Biotechnol. 34:242–250*, Copyright 2015, with permission from Elsevier

are much greater and more difficult to take into account, the mechanisms of interaction between cells and nanomaterials are not yet fully understood. Besides, numerous works (Chen et al. 2019; Ameen et al. 2021; Juárez-Maldonado et al. 2021) show the toxic effects of nanomaterials on living cells, which restricts their use in bioanalytical devices based on microorganisms.

The classical immobilization methods used in microbial biosensors are adsorption, capture, covalent binding or crosslinking. All these methods enable the use of nanomaterials as a supporting matrix for biomaterial immobilization. Herewith, nanomaterials link the active site of the enzyme or cell membrane with the electrode acting as conductors along which electrons are transferred to the electrode via nonconducting polymer materials. Nanomaterials affect the mechanical properties of the electrode (rigidity/elasticity) and create a biocompatible medium for immobilization of enzymes. Modification of nanomaterials by various functional groups enables stronger immobilization of biological objects on the electrode due to forming chemical bonds. For instance, the occurrence of hydroxyl (–OH) functional groups on the CNT surface contributes to adhesion of bacteria, because hydrogen bonds with bacterial cell walls form (Thepsuparungsikul et al. 2014). The maximum power of a biofuel cell based on an anode formed from a complex of multiwalled CNTs functionalized by –OH groups (MWCNT-OH) is 167 mW/m^2, which is 130% higher than for an anode from common carbon cloth. A looser netted dispersion and a rougher surface of MWCNT-based anodes enables bacteria to penetrate the inner layers of tubes, which increases the active area of the surface, enhances the colonization of bacteria at the anode and raises the efficiency of eliminating organic compounds from the sample at the biofuel cell functioning (Nosek et al. 2020).

The use of a carbon nanomaterial—graphene—enables the formation of 3-dimensional structures with high specific surfaces (Zou et al. 2016); herewith, introduction of CNTs (Tsai et al. 2015) or metal nanoparticles (Zhao et al. 2015b) into the graphene framework inhibits the aggregation of graphene sheets and additionally enhances the bond between them.

One of the problems in immobilization is to produce an oriented tie-in of the enzyme to the electrode surface, as well as to affect the distance between the enzyme's redox site and the electrode surface, to make the distance minimal. This is important for electron transfer between components of the system. Nanomaterials enable an oriented immobilization of biomaterial on the electrode, which makes it possible to avoid denaturation of the enzyme, to preserve its affinity and bioactivity, providing herewith for a decrease of the space between the enzyme's active site and the electrode. Thus, the use of CNTs in combination with bifunctional copolymer containing pyrene and activated ester groups for crosslinking and tethering has been shown (Gross et al. 2016) to significantly improve the quality of laccase immobilization owing to the formation of a hydrophobic site of binding in immediate vicinity to the laccase T1 site. This immobilization technique enables regulating the orientation of the enzyme on the electrode due to the formation of amide bonds. The thus formed biocathode makes it possible to significantly increase (as compared with laccase immobilization by simple physical sorption) catalytic currents of oxygen reduction. For this design of biocathode the maximum current density is 170 mA/cm^2 together with the high efficiency of electron transfer.

The possibility of using a nanocomposite film, consisting of glucose oxidase immobilized on Fe_3O_4 nanoparticles dispersed in chitosan, approximately 22 nm in diameter, for detection of glucose in the absence of a mediator, has been shown in Kaushik et al. (2008). Herewith, Fe_3O_4 nanoparticles provide not only a high electroactive surface area but also contribute to the oriented immobilization of the enzyme. Incorporation of paramagnetic Fe_3O_4 particles into polyelectrolyte microcapsules with the enzyme urease enabled forming a bioreceptor on the surface of the electrode without additional reagents, using a magnetic field (Reshetilov et al. 2016). This made it possible to avoid chemical modification of the electrode surface for immobilization of the enzyme and to provide for a fast regeneration of the electrode after a measurement cycle.

The works of Ahmad and Sardar (2015) and Ding et al. (2015) have considered advantages and disadvantages of nanoparticles as an enzyme immobilization matrix. As practice shows, refinement of biological objects' immobilization using nanomaterials is not yet a fully predicted effect and requires further research into the mechanism of the process, especially in the case of microorganisms.

Long-term stability of biomaterial

Immobilization on nanomaterial enables not only retaining enzymes or cells on the surface of the electrode but also creating a microenvironment, i.e., a medium in which a biological component preserves its activity for a long time (Ansari et al. 2009; Zhang and Cai 2019; Magro et al. 2020). Examples to show the preservation of biomaterial activity at a sufficiently high level using nanomaterials are given in Table 1. Herewith, it should be noted that nanomaterials may have a toxic action on enzymes and microorganisms (Mohanta et al. 2019; Peng et al. 2020). A rule follows from this fact that, prior to application, nanomaterials are specially modified to eliminate/reduce the toxic effect (Papadopoulos et al. 2019). Thus, modification may change the solubility of nanomaterials (Negm et al. 2020), their electrochemical (Zhao and Stoddart 2009) and mechanical (Zhang and Huang 2016)

Table 1 Application of nanomaterials for improving the long-term activity of biosensors and biofuel cells

Biomaterial	Substrate	Composite with nanomaterial/biosensors or biofuel cells	Lifetime	Drop of activity, % of initial value	References
Laccase	Bisphenol	Bacterial cellulose/carboxylated MWCNTs/zeolitic imidazolate framework-8 (ZIF-8)/biofuel cell	20 days	80	Li et al. (2020b)
Glucose dehydro-genase	Glucose	Thionine and gold nanoparticles grafted on aminocarbon nanotubes/graphene support/biofuel cell	4 weeks	60	Navaee and Salimi (2018)
Glucose oxidase	Glucose	3-Dimensional graphene/biofuel cell	7 days	60	Babadi et al. (2019)
Glucose oxidase	Glucose	Graphene nanoplates/ZnO nanowires/biosensor	30 days	100	Rafiee et al. (2020)
Catalase	Hydrogen peroxide	Iron nanoparticles coated with graphene layers supported on multiwalled carbon nanotubes/biosensor	25 days	95.4	Soto et al. (2020)
Laccase	Polyphenols	Gold nanoparticles electrodeposited in a screen-printed carbon electrode modified with polypyrrole through in-situ electropolymerization/biosensor	1 month	85	Mohtar et al. (2019)
Glucose dehydro-genase	Glucose	MWCNTs coated with poly(methylene green)/biofuel cell	2 months 1 year	60 10	Tahar et al. (2019)
Microbial consortium collected in a Singapore wastewater treatment plant	Acetate, municipal wastewaters	MnO_2/MWCNTs/polyvinylidene fluoride/biofuel cell	1.5 years	50	Kharkwal et al. (2017)
Cholesterol oxidase	Cholesterol	Gold nanoparticles/MWCNTs/polypyrrole/biosensor	7 days	76	Alagappan et al. (2020)
Glucose oxidase	Glucose	Polyaniline/montmorillonite/platinum nanoparticles/biosensor	2 months	91.7	Zheng et al. (2020)

properties, their toxicity (Asghary et al. 2019; Norizan et al. 2020).

A detailed description of the properties of graphene—a view of its mechanical strength, high electron conductance, large specific surface, high porosity, i.e., the properties that can be used to facilitate direct electron transfer and to increase enzyme load in biosensors and biofuel cells—is given in Tang et al. (2020). Entrapment of the enzyme into a three-dimensional graphene matrix or its dense enclosing with nanomaterials evokes a stabilization of enzyme activity. The work of Babadi et al. (2019) has shown that the microporous structure of three-dimensional graphene (3DG) can prevent the denaturation of the immobilized enzyme, enzyme leaching, and provide a sufficient concentration of both glucose and oxygen to the enzymes. Figure 4 presents micrographs of glucose oxidase adsorbed on three-dimensional (3D) graphene. The use of such 3D structures is especially promising when creating microbial fuel cells (Chung and Dhar 2021; He et al. 2021). The porous structure of the anode based, e.g., on 3D graphene aerogel (GA) decorated with platinum nanoparticles, provides for not only internal colonization by bacteria and electron transport, but also the long-term activity of microbial catalyst (Zhao et al. 2015a, b).

Nevertheless, the question of how biological material is entrapped on the surface of a nanomaterial and how electrons are transferred in such structures still remains open and is actively investigated. This is primarily due to progress in

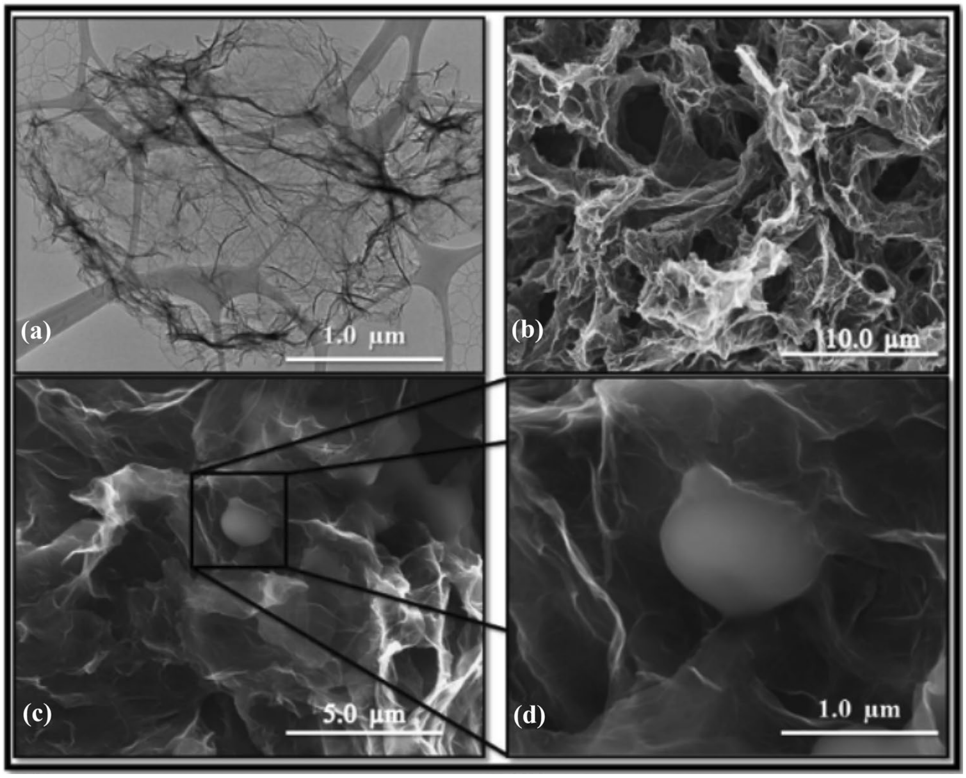

Fig. 4 A high resolution transmission electron microscopy (HRTEM) image of 3DG, **B** a field emission scanning electron microscopy (FESEM) image of 3DG, **C** the hybrid of GOx and 3DG and **D** immobilised GOx on 3DG. Reprinted from Babadi et al., *Int. J. Hydrog. Energy 44(57):30367–30374,* Copyright 2019, with permission from Elsevier

genome sequencing, transcriptomics and proteomics, bioinformatics, mass spectrometry methods, electrochemical methods of analysis etc.

Decrease of working potential of biosensor

The use of nanomaterials affects the electrochemical parameters of an analyzing device and enables registration at a decrease of the applied working potential during the generation of a signal by the biosensor. For instance, many bioelectrochemical devices use NAD-dependent dehydrogenases. In this case, the regeneration of the cofactor [the catalytic oxidation of the reduced form of β-nicotinamide adenine dinucleotide (NADH)] is one of the important reactions at the electrode. However, the electrochemical regeneration of NAD^+ (i.e., the oxidation of NADH formed during the enzymatic reaction) usually occurs at significant overvoltages. In fact, the oxidation of NADH has an overvoltage of about 1.0 V on glassy carbon electrodes and even higher on platinum surfaces, which restricts the use of these enzymes in biofuel cells and biosensors (Karyakin et al. 2003; Shao et al. 2010). Studies have shown that nanomaterials can reduce NADH oxidation overvoltages in NAD-dependent enzymatic fuel cells (Selloum et al. 2020). Application of silver nanoparticles enables shifting the NADH oxidation-peak potential to 0.574 V; herewith, the current increases twofold as compared with the nonmodified glassy carbon electrode (Aydoğdu Tığ 2017), which is well seen on cyclic voltammograms (Fig. 5) by the shift of the peak into the region of lower potentials at the modification of the electrode by nanomaterials. In the work of Aquino Neto et al. (2013), the use of MWCNTs led to NADH oxidation occurring between 0.14 and 0.16 V relative to Ag/AgCl. This

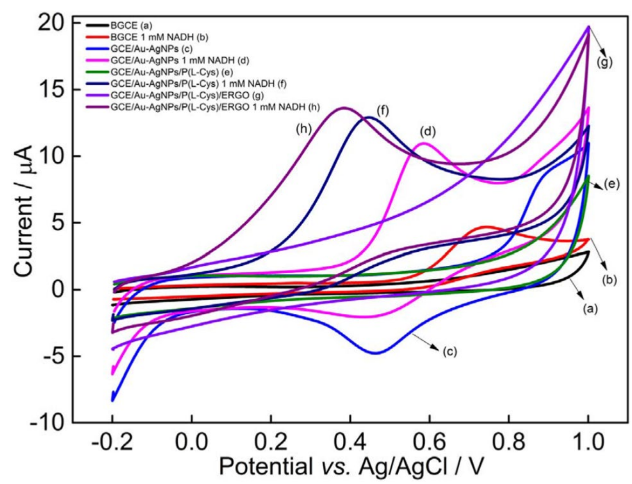

Fig. 5 Cyclic voltammograms of the bare glassy carbon electrode (GCE) (**a**, **b**), GCE/Au-AgNPs (gold-silver bimetallic nanoparticles) (**c**, **d**), GCE/Au-AgNPs/P(L-Cys) (poly(L-Cysteine) (**e**, **f**) and GCE/Au-AgNPs/P(L-Cys)/ERGO (electrochemically reduced graphene oxide) (g, **h**) in 0.1 M PBS (pH 7.0) without and with 1.0 mM NADH, respectively. Reprinted from Aydoğdu Tığ, *Talanta, 175:382–389,* Copyright 2017, with permission from Elsevier

enables fabricating an effective biofuel cell with a power of 88 μW/cm^2.

Phenylalanine is determined using the enzyme phenylalanine dehydrogenase, the cofactor of which is also NADH. The use of graphene to modify carbon electrodes decreases NADH-oxidation overvoltage due to a high density of edge-plane-like defective sites in graphene that provide for numerous active sites for electron transfer to NADH (Moreira et al. 2018). Application of graphene oxide in this biosensor enables assaying phenylalanine at an applied potential of 600 mV. Graphene oxide can be dispersed in an aqueous solution due to the large number of oxygen-containing groups, and then be evenly distributed on the electrode surface; this provides for a large number of sites on the edge plane for electrocatalytic oxidation (Fig. 6).

A biosensor based on alcohol dehydrogenase for detection of ethanol is presented in the work of Wang et al. (2019b). The use of single-walled CNTs and chloranil makes it possible to decrease the enzyme (NADH) cofactor oxidation potential down to 0.13 V. Such decreases of the working potential bring significant practical benefits. It is known that high supplied potentials lead to a fouling of the electrode by intermediate reaction products and reduce its service life. Thus, the use of nanomaterials decreasing the applied potentials makes it possible to increase electrodes' service lives.

As nanoparticles differ in their geometric parameters and physicochemical properties, their interaction with biological objects will vary significantly; knowledge in this field is currently being accumulated for further practical application.

Mediator-free electron transfer

In practical application of biosensors and biofuel cells, it is important for the reactions to be reagent-free, without the need to introduce additional compounds when making assays. The active site of a biocatalyst (enzyme, cell, etc.) and the electrode can be considered as a donor–acceptor pair with a movement of electrons between them. Electron transfer in bioelectrochemical devices is carried out by two mechanisms—indirect mediated transfer (e.g., by means of special redox mediators) (MET) and direct electron transfer, i.e. without mediators (DET). It is often very difficult to make a clearcut distinction between DET and MET due to the complexity of the underlying mechanisms, especially if the whole cell acts as a biocatalyst (Schröder 2018). Sometimes it is determined by the transfer of electrons by enzyme's cofactors, and though no redox mediator is added, the redox cofactor acts as a mediator. One of the criteria of direct transfer is that enzyme's cofactor(s) remains bound to or is associated with the enzyme during the electron transfer. It is for this reason, for instance, that nicotinamide adenine dinucleotide (NAD)-dependent enzymes are not considered to be involved in direct electron transfer, whereas NAD cofactor freely diffuses and does not bind to the enzyme (Milton and Minteer 2017). Enzymes, which can perform a direct electron transfer to the electrode via an electroactive subdomain in its structure, do occur in nature; this effect is characteristic of enzymes with a metal in their composition. For instance, laccase and bilirubin oxidase comprise several sites containing copper, and, during the oxidation of substrates, electrons can be transferred via them to the electrode (Shleev et al. 2005; Brocato et al. 2012). A tentative scheme of this process for laccases is given in Fig. 7A. The site T1 was shown to be the main acceptor of electrons from carbon electrodes during the heterogeneous reduction both under aerobic and anaerobic conditions. Electrons are transferred from the electrode to the site T1 of the adsorbed enzyme, and then, via the mechanism of intraprotein electron transfer, to the cluster T2/T3, where molecular oxygen is reduced to water. At the same time, when using gold electrodes, the main electron acceptor is the site T2 (Fig. 7B).

Application of nanomaterials makes it possible in some cases to immobilize the enzyme in an oriented way, which is hard to predict theoretically but enables in practice an efficient transfer of electrons from the enzyme to the electrode surface without using additional reagents due to decreasing the distance between the enzyme's active site and the electrode surface (Lim et al. 2007; Yu and Myung 2021).

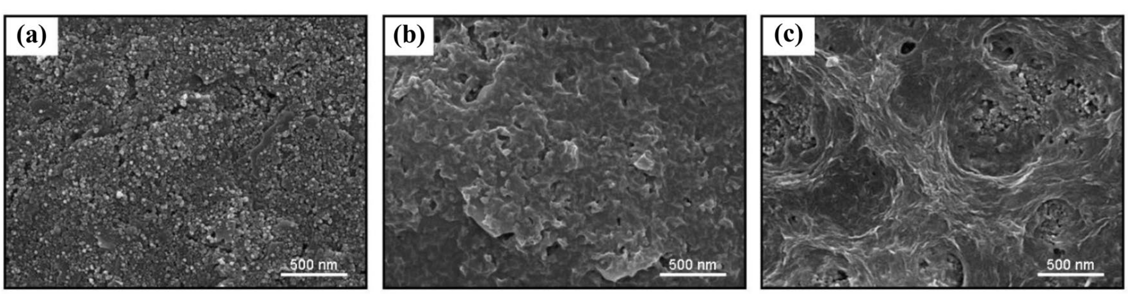

Fig. 6 SEM images of SPCEs (**A**), GO/SPCEs (**B**) and rGO/SPCEs (**C**). Graphene oxide (GO); screen-printed carbon electrodes (SPCEs); reduced Graphene Oxide (rGO) modified SPCEs (rGO/SPCEs). Reprinted from Zhang et al. (2011), *Int. J. Electrochem. Sci. 6:819–829,* Creative Commons Attribution 4.0 International License

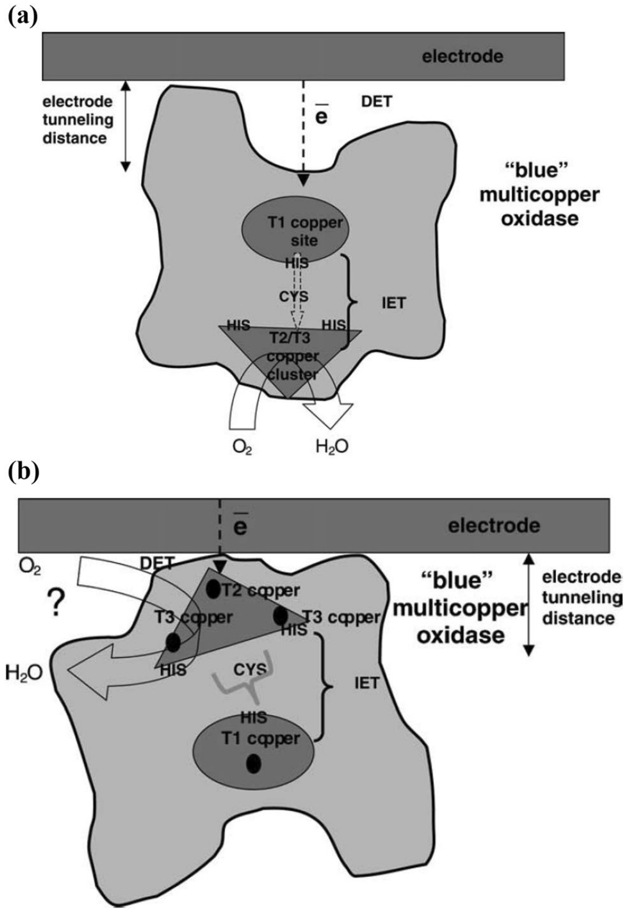

Fig. 7 **A** Proposed scheme for electroreduction of oxygen at carbon electrodes with adsorbed multicopper oxidase. **B** Proposed scheme for electrocatalytic activity of some oxidases on the gold electrode. Reprinted from Shleev et al., *Biosensors and Bioelectronics, 20(12), 2517–2554,* Copyright 2005, with permission from Elsevier

Nanomaterials also provide close physical contact between the biocatalyst and the electrode, which enables the electron to freely pass to the electrode. The use of titanium nanoparticles in combination with laccase, as it is shown in Zhou et al. (2015), not only increases the registered electrocatalytic activity of the enzyme as a catalyst of oxygen reduction on the biofuel-cell cathode, but also contributes to the direct transfer of electrons in the absence of mediators.

Hydrogenases have metals in their composition, which also provides for the direct transfer of electrons to the electrode and expands the use of bioelectrochemical devices on their basis (Bollella et al. 2018). Additional oriented immobilization using nanomaterials, in particular CNTs, amplifies the direct bioelectrocatalytic signal from the enzyme during the oxidation of hydrogen (Lojou et al. 2008; Ruff et al. 2018).

Mediator-free electron transfer has been shown for many oxidoreductases that have nonmetal cofactors, such as flavin adenine dinucleotide and pyrroloquinoline quinone. The use of nanomaterials makes it possible to register the signal in the absence of mediators for glucose oxidase (Zhang et al. 2011), glucose dehydrogenase (Adachi et al. 2020), fructose dehydrogenase (Bollella et al. 2019), cellobiose dehydrogenase (Tavahodi et al. 2016).

Table 2 presents some examples of nanomaterial-modified biosensors and biofuel cells for detection of various analyzed substances without using electron transfer mediators with indicated values of electron transfer rates.

Some bacteria have been shown to be capable of direct electron transfer via cell membranes to the electrode, which makes them attractive for bioelectrochemical systems (Koch and Harnisch 2016). Most likely, DET is carried out using outer membrane cytochromes, conductive pili or self-assembled appendages called nanowires (Reguera 2018; Aiyer 2020). Nanowires are an aggregate of various cytochromes, periplasmic proteins and outer membrane proteins (Sure et al. 2016). Artificial nanowires (metal and graphite nanoparticles) can contribute to the formation of electron bridges across the periplasm or lipid membranes, via which the electron passes to the electrode, and the bioelectrochemical device generates a signal (Wu et al. 2011; Zhao et al. 2015a). The proposed pathways of electron transfer from the cell to the electrode in the presence and absence of cell-bound nanoparticles on the example of palladium nanoparticles (Pd0) are shown in Fig. 8 as exemplified by palladium (Pd^0) nanoparticles. Most likely, the charge transfer using nanoparticles of another class will be carried out by a completely different mechanism, since the interaction of cells and nanomaterials depends very much on the physical, chemical, etc. properties of the class of nanomaterials used, as well as the physiological characteristics of the applied microorganism.

To implement DET, the physical contact of the outer membrane cytochromes with the electrode is necessary, therefore, the use of nanomaterials allows contact with the electrode not only to the monolayer of bacteria directly lying on the surface of the electrode, but also to cells located in the bulk of the biofilm, far from the electrode. The possibility of creating three-dimensional electrodes based on a conductive network of nanomaterials can provide impressive analytical characteristics—the ability to receive a signal from a larger number of cells, which is especially important when creating microbial biofuel cells to increase their power (Chung and Dhar 2021; Mashkour et al. 2021).

The synthesis of nanoparticles by cells leads to the possibility of using these cells with synthesized nanoparticles to create a biosensor. It has been shown that nanoparticles sediment in the perimembrane surface of the cells, which leads to a current rise (Jiang et al. 2014).

In the work of Anwer et al. (2019), it has been shown that a modification of the felt cathode (Mn/CF) by manganese dioxide (MnO_2) using the electrodeposition method leads to an amplification of extracellular electron transfer;

Table 2 Examples of enzymatic biosensors and biofuel cells based on mediator-free electron transfer

BM	Substrate	Composite with nanomaterials	Electron transfer rate	Michaelis–Menten constant	Power (for biofuel cells)	References
Glucose oxidase	Glucose	CNTs/polyethyleneimine/Ag nanoparticles/naphthalenethiol	$9.6 \pm 0.4\ s^{-1}$	0.51 ± 0.04 mM	$1.46 \pm 0.07\ mW\ cm^{-2}$	Christwardana et al. (2018)
Alcohol dehydrogenase	Glycerol and glycer-aldehyde	Gold nanoparticles modified with 4-aminothiophenol	$65 \pm 13\ s^{-1}$	3.5 mM for glycerol and 11.8 mM for glycer-aldehyde	$130\ \mu W\ cm^{-2}$	Ratautas et al. (2017)
Nitric oxide reductase	Nitric oxide	Carboxylated single-walled carbon nanotubes/lipidic bilayer [1,2-di-(9Z-octadecenoyl)-sn-glycero-3-phosphoethanolamine, 1,2-di-(9Z-octadecenoyl)-3-trimethylammonium-propane, 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-polyethylene glycol]	$1.96 \times 10^{-4}\ cm/s^{-1}$	4.3 µM	–	Gomes et al. (2019b)
Glucose oxidase	Glucose	Reduced graphene oxide covalently conjugated to magnetic nanoparticles (Fe_3O_4)	$13.78\ s^{-1}$	0.16 mM	–	Pakapongpan and Poo-arporn (2017)
Nitric oxide reductase	Nitric oxide	MWCNTs/1-n-butyl-3-methylimidazolium tetrafluoroborate	$0.35\ s^{-1}$	2.17 µM/L	–	Gomes et al. (2019a)
Hemo-globin	Nitro-methane	Three-dimensional graphene–nitrogen doped carbon nanotubes composite	$7.12\ s^{-1}$	300 µM/L	–	Wang et al. (2018)
Glucose oxidase	Glucose	CNTs	$1.22\ s^{-1}$	6.53 ± 0.58 mM	–	Liu et al. (2018)
Glucose dehydrogenase	Glucose	Polyaniline, gold nanoparticles and cysteamine-modified gold electrode		14.7 mM	–	Gineitytė et al. (2019)

a direct extracellular electron transfer for this system has been observed. The obtained data demonstrate that MnO_2 interacts electrochemically with microbial cells. This cathode was used for microbial electroreduction of CO_2 to biofuels, where anaerobic silt acted as a biocatalyst.

Nevertheless, the exact mechanisms of electron transfer have been studied insufficiently well for most known exoelectrogens, and the mechanisms of charge transfer via nanoparticles still need to be actively investigated.

Increase of assay sensitivity

The use of nanomaterials leads to a change of biosensor's analytical characteristics, e.g., an increase of the assay sensitivity (Wu et al. 2020). A review (Olayiwola et al. 2020) reports on the poly (propylene imine) dendrimer. This polymer possesses a large surface area, has numerous functional groups via which it binds to biological components; herewith, it can act as a nanomediator and finds wide application

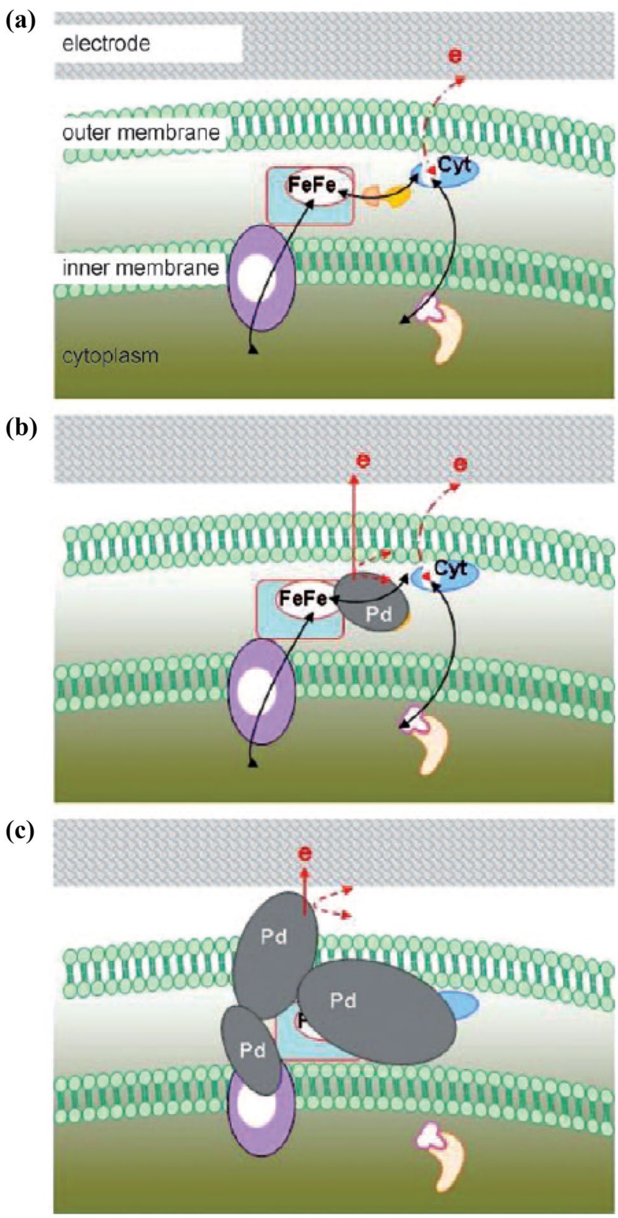

Fig. 8 Hypothesized pathways for the extracellular electron-transfer chain between the cell and the electrode: **a** in the absence of Pd^0 (via periplasmic cytochromes and hydrogenases); **b** in the presence of Pd^0 at a low loading; **c** in the presence of Pd^0 at a high loading. [FeFe] is an iron-only hydrogenase, Cyt is c-type cytochrome, and areas shaded gray are the Pd^0 nanoparticles. Reprinted from Wu et al., *Angew. Chem. 123:447–450*, Copyright © 2011 WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim

in electrochemical biosensors for detecting target biomolecules with high selectivity and sensitivity. Modification of the biosensor's measuring electrode with poly(propylene imine) dendrimer and CdTe/CdSe/ZnSe quantum dots leads to an increase of the cholesterol detection limit up to 0.075 mM and an assay sensitivity of 111.16 μA mM^{-1} cm^{-2} (Mokwebo et al. 2018). The biosensor is stable for over a month and possesses a high selectivity with respect to the cholesterol molecule.

Modification of a microbial biosensor based on *Gluconobacter oxydans* using MWCNTs enables increasing the sensitivity of the biosensor fourfold at the registration of glucose and fivefold in the case of ethanol as compared with the nonmodified biosensor; herewith, the maximum signal increases 14 times at the detection of glucose and 6 times for ethanol (Plekhanova et al. 2019).

In the work of Wang et al. (2019a), hybrid microspheres with gold nanoparticles are used to modify electrodes with cholesterol oxidase. The use of nanoparticles enables increasing the signal 13-fold as compared with the control electrode, which leads to an increase of the cholesterol assay sensitivity, whose detection limit is 50 μM.

The use of a graphene–poly(3-aminobenzoic acid) composite for modification of electrodes has been shown to increase the signal approximately 16-fold as compared with the signal of an electrode without this nanocomposite (Pothipor et al. 2019). A higher signal is found to be produced when using porous nanoparticles as a label as compared with common gold nanoparticles, and the sensitivity to the prostate specific antigen increases 120-fold as compared with the sensitivity when using standard gold nanoparticles. Using this component, the detection limit of 0.13 pg/mL is obtained, which is four orders of magnitude higher than the clinically significant level in human blood serum.

The simultaneous use of nanomaterials of various chemical origin makes it possible to change the sensitivity of biosensors or biofuel cells on their basis. In the work of Hossain and Park (2017), glucose oxidase is immobilized on multilayer reduced graphene oxide sheets decorated with platinum and gold flower-like nanoparticles. This electrode is, first, flexible; second, it shows a high electrocatalytic activity with respect to the oxidation of hydrogen peroxide (the sensitivity is 506.25 μA/mM cm^2) and, respectively, to the detection of glucose (the sensitivity is 17.85 μA/mM cm^2). The electrode has a wide linear range both for hydrogen peroxide detection (0.5–8 mM) and for glucose detection (0.01–8 mM). Herewith, the biosensor response time does not exceed 3 s.

The increase in the sensitivity of devices based on nanomaterials is associated, firstly, with an increase in active surface area, which leads to an increase in the effective concentration of the biocatalyst on the surface of the electrode, and secondly, with a decrease in the electrode resistance due to a rise in the number of reduced charge carriers. Besides, the directed immobilization of the biocatalyst facilitates the interaction of the enzyme's active centre with the electrode, which also affects the sensitivity of the device on the whole. In the work of Fu et al. (2021), a new mechanism has been proposed and experimentally confirmed in which electron transfer is physically accelerated inside nanostructured electrodes due to a decrease in charge shielding, which leads to an increase in biosensor sensitivity. Based on this mechanism and tests of various structures of nanoporous electrodes, the possibility of tuning electrochemical sensors in terms of signal amplification, limits of detection or other performance indicators was demonstrated. The high sensitivity and output signal of nanoporous gold electrodes compared with flat gold surfaces may be a consequence of the reduced Debye volume and the reduced effect of charge shielding in these nanopores.

Application of nanomaterials enables affecting the affinity of enzymes to substrate. The Michaelis–Menten constant represents one of the most important parameters of enzymatic reaction kinetics and is a measure of chemical affinity of substrate to enzyme (Cornish-Bowden 1979). The lower its value, the greater affinity the substrate has to the enzyme. In the work of Mirzaei et al. (2019), the apparent Michaelis–Menten constant for the enzyme lactate dehydrogenase immobilized on a glassy carbon electrode via hydrophobin–graphene oxide nanocomposite is shown to be lower than for the free enzyme. This decrease of the value of the constant is accompanied with an increase of the electrode signal due to the increase of the surface and a rise of conductance of the used composite. The same effect of the nanomaterial is shown in the work of Buk and Pemble (2019). The enzyme glucose oxidase is immobilized on a nanohybrid material from carbon quantum dots and gold nanoparticles. The apparent Michaelis–Menten constant is 2.93 mM against 27 mM for free glucose oxidase. Herewith, the biosensor possesses an increased sensitivity to glucose (626.06 μA mM^{-1} cm^{-2}). Nevertheless, at a clearly positive action an opposite effect can be also observed; in the work of Plekhanova et al. (2019), the apparent Michaelis–Menten constant is shown to increase at a modification of the electrode by nanomaterials despite an increase of the sensitivity of the biosensor to substrate. In the case of glucose dehydrogenase, the affinity to substrate decreases 3.5-fold; in the case of alcohol dehydrogenase, 1.3 times. Possibly, a decrease of the value of the constant occurs when the immobilized and free enzymes are compared, and in the case of an enzyme immobilized with or without a nanomaterial, the comparison would have been not in favour of the nanomaterial, either. Unfortunately, most works compare the enzyme immobilized with nanomaterials with the free enzyme. In such cases, the change of the value of the constant could be due not to the presence of a particular nanomaterial but only to the immobilization method.

Use of nanomaterials as labels in immunosensors

Nanomaterials can be used as labels in immunosensors, acting as an alternative to classical enzymatic tags (Iglesias-Mayor et al. 2019). Two strategies of nanoparticle detection can be considered here—either direct detection (change of metal valence in nanoparticles during the process under the action of an electric field) (Fig. 9A) or the use of nanoparticles as a catalyst of redox processes at the electrode (e.g., as an H_2O_2 reduction catalyst, Fig. 9B). Examples of immunosensors using nanomaterials are given in Table 3. As many nanoparticles possess redox properties, they can be easily determined using electrochemical methods without additional stages after the antibody–antigen immunoreaction is completed. Various nanomaterials—they are called nanozymes—have been shown to mimic the activity of natural enzymes, such as peroxidase, catalase, oxidase, superoxide dismutase (Cormode et al. 2018; Huang et al. 2019; Singh 2019; Demkiv et al. 2021). Nanomaterials with a peroxidase-like activity are widely used as an alternative to the enzyme horseradish peroxidase, one of the most widely used labels in immunosensors. In particular, in the presence of gold nanoparticles the hydrogen ion reduction potential shifts to less negative values. Correspondingly, at a certain supplied potential, hydrogen ions would be reduced only in the presence of these nanoparticles. Using these nanoparticles as antigen or antibody labels, a corresponding analyte in the investigated sample can be found (Maltez-da Costa et al. 2012; Sun 2015; De Oliveira et al. 2018).

Currently, methods of immunoassay are being actively worked out due to the development of personalized medicine, conducting tests at home, without the involvement of highly qualified personnel. New express methods make it possible to obtain accurate quantitative data on the simultaneous determination of several substances in multicomponent samples. For this reason, this area of research attracts considerable attention and is aimed at creating simple, portable and inexpensive biosensors for individual use. Since an important part of the immunobiosensor is the biorecognition molecule, the main efforts are aimed at obtaining highly specific antibodies with low cross-activity against related antigens, as well as at developing methods to obtain conjugates of antibodies with nanomaterials.

Catalyst of electrooxidation

Nanoparticles with peroxidase activity can be used not only in immunoanalysis as a label but also in the development of enzyme biosensors or fuel cells, replacing one of the enzymes in cascade reactions (Fig. 10). For instance, the peroxidase activity of Co_3O_4 nanoparticles was used in the development of an efficient platform for detecting hydrogen peroxide and glucose, using glucose oxidase for oxidation of glucose (Jia et al. 2016). One of the most effective nanozymes (nanoparticles imitating natural enzymes) that can replace peroxidase are Prussian blue nanoparticles (Vokhmyanina et al. 2020).

A combination of several nanomaterials of the same class or even several classes could effectively detect hydrogen

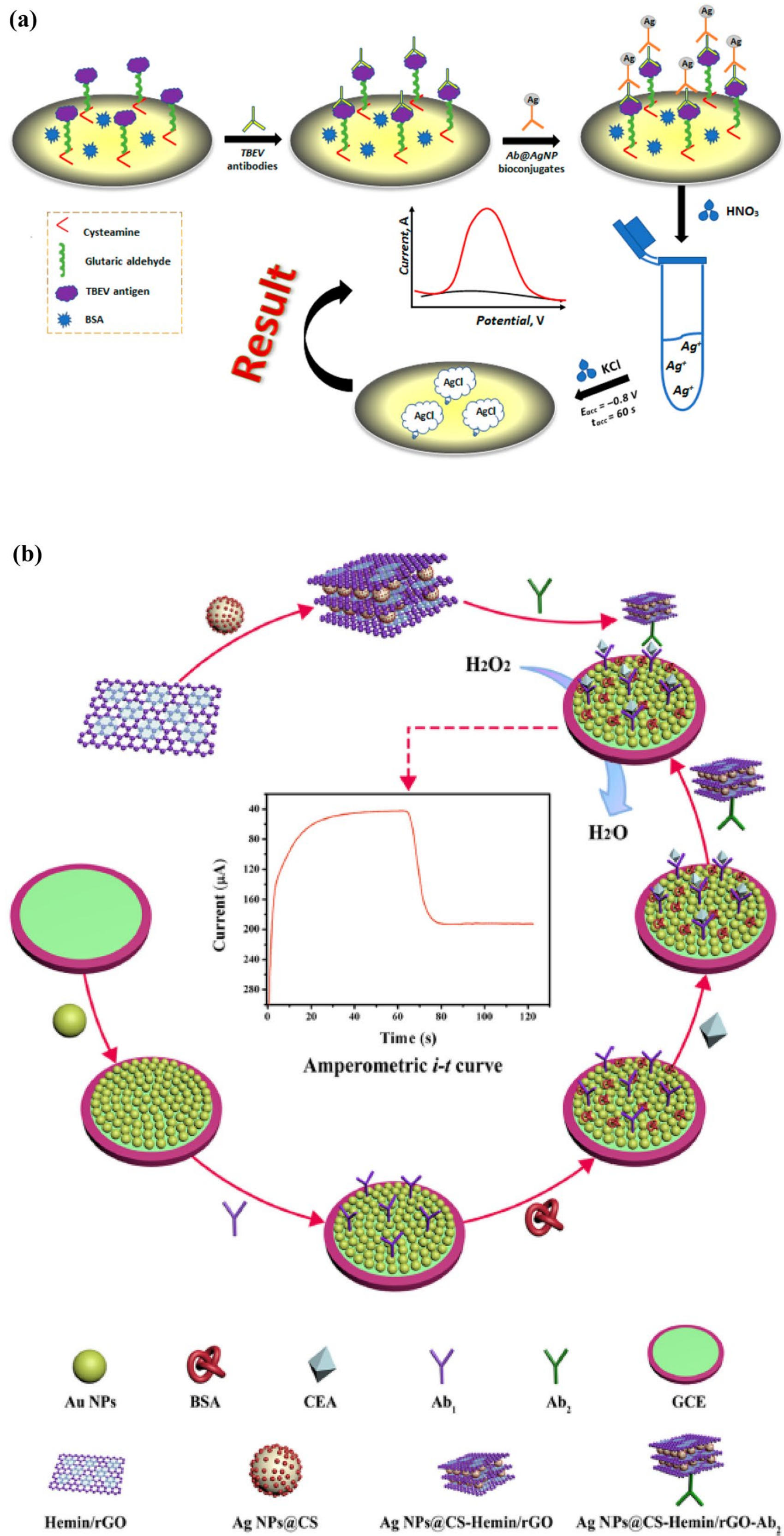

Fig. 9 **A** Scheme of the electrochemical immunosensor preparation and principle of antibody detection based on the direct detection of the label. Reprinted from Khristunova et al., *Sensors 19(9):2103*, Copyright 2019. Creative Commons Attribution 4.0 License. Published by Multidisciplinary Digital Publishing Institute. **B** The procedure of sandwich-type immunosensor working electrode based on the use of the label as a hydrogen peroxide reduction catalyst. Reprinted from Zhang et al., *Biosensors and Bioelectronics, 126:785–791*, Copyright 2019, with permission from Elsevier

Table 3 Examples of using nanomaterials as labels in immunoassay-based biosensors

Type of label	Label	Assay format	Analyte	Sample	Detection limit	References
Electroactive	Gold nanoparticles	Sandwich	*Salmonella typhimurium*	Milk	7.7 cells mL^{-1}	De Oliveira et al. (2018)
	Silver nanoparticles	Sandwich	Antibodies to tick-borne encephalitis virus	Immuno-logical products	50 IU·mL^{-1}	Khristunova et al. (2019)
	Silver nanoparticles	Sandwich	Dengue biomarker NS1	Human blood serum	0.5 ng/mL	Awan et al. (2020)
	CdSe@ZnS quantum dots	Sandwich	Human immuno-globulin G	Buffer solution	3.5 ng/mL	Medina-Sánchez et al. (2016)
	Ni@Cd quantum dots	Sandwich	Prostate-specific antigen	Human blood serum	0.45 ng/mL	Ehzari et al. (2020)
	CeO_2–MoS_2–Pb^{2+} nanoparticles	Sandwich	Carcinoembryonic antigen	Human blood serum	0.3 pg/mL	Li et al. (2020a)
Electrocatalytic	Gold nanoparticles	Competitive	Tetrabromobisphenol A bis(2-hydroxyethyl) ether (TBBPA-DHEE)	Tap water, river water, water samples from halogenated antipyrene production	0.12 ng/mL	Dong et al. (2019)
	Silver nanoparticles	Sandwich	Carcinoembryonic antigen	Human blood serum	6.7 fg/mL	Zhang et al. (2019)
	Rh core and Pt shell nano-dendrites loaded onto amino group-functionalized graphene nano-sheet	Sandwich	Hepatitis B surface antigen	Human blood serum	166 µg/mL	Pei et al. (2019)
	Palladium nanoparticles	Sandwich	Prostate-specific antigen	Human blood serum	0.03 pg/mL	Dai et al. (2019)
	Iridium nanoparticles	Sandwich	Carcinoembryonic antigen	Human blood serum	0.23 pg/mL	Miao et al. (2017)
	Fe_3O_4 nanoparticles	Sandwich	Prostate-specific antigen	Human blood serum	18 fg/mL	Li et al. (2019)
	Molybdenum disulfide–copper oxide hybrid with gold nanoparticles	Sandwich	Alpha-fetoprotein (tumour marker for revealing adult primary liver cancer)	Human blood serum	0.037 pg/mL	Ma et al. (2019)

peroxide released during the reaction on the electrode. Thus, bimetallic PtRu (nPtRu) nanoparticles in combination with alcohol oxidase and methylamine oxidase are used to create amperometric biosensors for detection of primary alcohols and methylamine (Stasyuk et al. 2019). It has been shown that the replacement of peroxidase by nanoparticles leads to an increase in the linear detection range of analytes.

In the work of Inamuddin et al. (2020) nanoparticles of ZnO together with CNTs have been used for immobilization of glucose oxidase on the biofuel-cell anode. This nanocatalyst exhibited a higher electrocatalytic activity with respect to oxidation of glucose with a maximum current density of 4.9 mA/cm^2 at an uptake of glucose at a concentration of 50 mM in a phosphate buffer saline. CNTs also possess a catalytic activity to contribute to the redox reaction of hydrogen peroxide formed during the enzymatic reactions with the substrate, which also enables using them as a replacement of one of the enzymes in the biosensor (Lin et al. 2004). In the work of Díaz Nieto et al. (2018), an enzyme biosensor based on soybean peroxidase and chemically reduced graphene oxide provides for the direct electron transfer between the enzyme and the electrode, exhibiting a high affinity to hydrogen peroxide. Quantum dots are often used in optical biosensors, but there are examples of electrochemical biosensors where they are also used to increase the effective enzyme immobilization surface area, electron transfer and as an electrooxidation catalyst (Du et al. 2008).

The ability of nanoparticles to catalyze reactions by interacting with substrates and reactions is determined by the occurrence of coordination-unsaturated atoms at the surface, edges and corners of nanoparticles as compared with the total number of atoms (Navalón and García 2016). The authors report that, in particular, the atoms located at steps, corners and edges of nanoparticles exhibit the highest

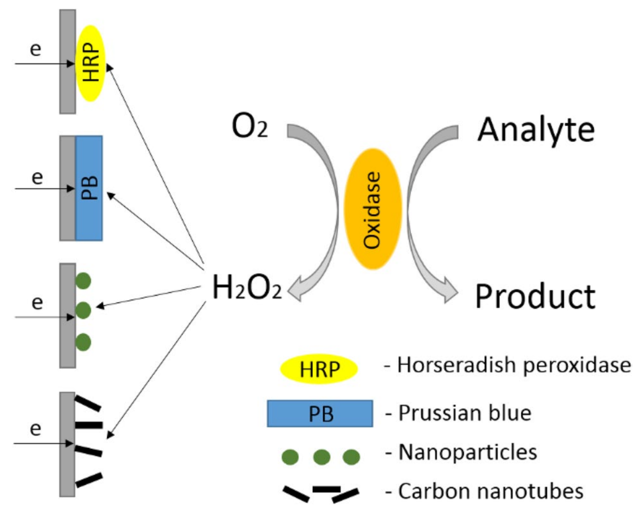

Fig. 10 The functioning principle of oxidase-based enzymatic biosensors

catalytic activity due to their low coordination number and their high tendency to increase this number by coordinating with substrates and other species in the surroundings. The electrical properties of nanomaterials are related to the quantum-dimensional effect and the effect of quantum confinement (Ramalingam et al. 2020). Different materials can change their properties when reduced to nanosize, e.g., copper loses its conductivity when producing nanoforms (Pan et al. 2019), and silicon dioxide, on the contrary, becomes conductive (Mehonic et al. 2016). For nanowires and nanotubes, it is characteristic that with a decrease in diameter below 20 nm due to an increase in the surface scattering of electrons and phonons, an increase in surface area and a very high density of electronic states, the conductivity increases sharply compared to bulk materials (Nandi et al. 2013; Buzea and Pacheco 2018). Thus, the reduction of structures to nanosizes leads to a decrease in resistivity and an increase in conductivity, which is important for bioelectrochemical devices.

In bioelectrochemical devices, the replacement of one of the enzymes by a nanomaterial enables a more accurate selection of the conditions for the functioning of a biocatalytic device on its basis. Nanomaterials, unlike enzymes, have a higher stability, strength, and have a lower cost. It has been shown that some materials even have more than one enzyme activity. For example, materials based on molybdenum disulfide (MoS_2) possess a peroxidase-like activity, catalase-like activity and superoxide dismutase activity (Xu et al. 2021). Thus, the use of nanomaterials as a substitute for enzymes is a promising trend of research (Alvarado-Ramírez et al. 2021).

At the same time, the use of nanomaterials instead of enzymes leads to an increase in the working potential of the electrode and to a slower electrode kinetics. Absorption of intermediate oxidation products on the electrode leads to the block of its activity. Besides, nanomaterials have a lower selectivity as compared with enzymes, and also require specific operating conditions (Thatikayala et al. 2020; Hassan et al. 2021). An interesting direction of research would be to compare the effect of replacing an enzyme with a nanomaterial on the long-term operation of the resulting device.

The main problems associated with the use of nanomaterials in biosensors and biofuel cells

Despite the widespread use of various nanomaterials for the modification of biosensor and biofuel-cell electrodes and the enormous fundamental-science significance of these studies, there are some practical aspects that should be taken into account. Thus, the processes of nanoparticles' synthesis and of biocatalyst immobilization into nanoparticles during the development of bioelectrochemical devices are rather complex and labour-intensive, which significantly reduces the practical value of the systems being developed. Besides, the use of nanomaterials is associated with complex and multi-stage processes of biocatalyst immobilization on the electrode as part of a nanocomposite, which complicates the practical use of the developed laboratory techniques and creates difficulties associated with industrial use.

Another important problem is related to the implementation of the electron transfer process in biocatalytic systems. There are works in which the fundamentals of the phenomenon of electron transfer reactions in redox enzymes, most widely used for the development of biosensors and enzyme fuel cells, are considered in detail (Bollella and Katz 2020). Theoretical aspects of DET-type enzyme bioelectrocatalysis, the significance of nanostructures as scaffolds for DET-type reactions, protein engineering approaches for DET-type reactions (Adachi et al. 2020) have been developed. Attempts are being made to study the mechanisms of electron transfer not only between enzymes and electrodes, but also between microbial cells and electrodes in microbial fuel cells (Aiyer 2020). In the case of microorganisms, electrical conductivity control is associated not only with physiological changes and internal reactions during electron transfer, but also with a number of particular factors and parameters (e.g., intercellular interaction), which are more difficult to account for than in the case of individual enzymes. As an example, we can cite such a field of activity as the synthesis of nanomaterials using biological objects. For instance, dissimilatory metal reduction bacteria, especially *Shewanella* and *Geobacter* species, are capable of extracellular electron transfer. Over the past decade, significant progress has been made in studies of the mechanisms underlying such electron transfer using electron acceptor electrodes, but understanding how this electron transfer participates in the formation of inorganic nanoparticles is still in its infancy (Zou et al. 2021).

As a rule, when studying the process of charge transfer in electrochemical devices, two main mechanisms are distinguished—relay-race and hopping (Habermüller et al. 2000; Arlyapov et al. 2021). Despite the general progress in elucidating the mechanism of electron transfer for many redox enzymes, some enzymes are still under the close attention of researchers; and it is yet remains to be elucidated how, by what mechanisms the interaction between various enzymes and microorganisms occurs, what happens to these processes during biological mutations. On the whole, understanding the charge transfer mechanisms and their role in the vital activity of the cell will contribute to the creation of practically important devices with improved characteristics.

Conclusions

The use of nanomaterials for modifying biosensors and biofuel cells is currently the most developed direction of research. Most publications discuss improvements of the characteristics of the developed device at its modification by a nanomaterial or a composite including several nanomaterials. The main effects of a nanomaterial are associated with its physical characteristics—a greater surface area to volume ratio, which leads to an increase of the electrode's effective area and an improvement of the analytical characteristics of the device. This yields a more efficient immobilization of the biocatalyst on the signal-converter surface enabling in some cases an orientation of the biocatalyst with respect to the electrode surface. The biocompatibility of nanomaterials makes it possible to create a microenvironment maintaining the biocatalyst in active stage for a long time. The high conductance of nanomaterials leads to an enhanced charge transfer between the biocatalyst and the electrode, enabling the direct transfer without using additional reagents. All this ultimately expands the spheres of use of nanomaterial-based biosensors and biofuel cells.

A high surface area to volume ratio characteristic of nanomaterials makes possible a decrease in size of electrochemical devices. In the process of developing biosensors and biofuel cells, one can observe a trend of moving from macro devices through micro- to nano constructions. Combining biosensor developments with microelectronic technologies makes it possible to produce analytical-type micro- and nanodevices. Such devices are less traumatic when embedded in living organisms (Gamella et al. 2018; Ibrahim et al. 2021). The development of conducting gels based on nanomaterials enables changing the mechanical properties of materials and creating flexible electrodes. They can be formed into tattoos on human skin or flexible wearable biosensors and biofuel cells for real-time invasive or noninvasive monitoring of biologically significant molecules (Mathew et al. 2021).

The diversity of nanomaterials and conducting polymers leads to their virtually unlimited combinations for creating biosensors and biofuel cells. Both the overall efficiency of a device, as well as particular parameters of the bioelectrochemical system can be changed.

Thus, to develop a strategy for the use of nanomaterials, it is necessary, first, to ensure a controlled composition of the resulting nanomaterials with reproducible properties, dimensions and stability during their production. Second, when using nanomaterials to modify electrochemical devices, it should be remembered that they affect all the analytical characteristics of the device, i.e., their effect is integrated. Therefore, it is necessary to develop a general scheme for the use of nanomaterials and to compare the developed biodevices for all analytical parameters with nanomaterials and without them under the same conditions, in order to more accurately determine the influence of particular nanomaterials. Thirdly, the use of nanomaterials as part of bioelectrocatalytic devices not only expands the scope of their application, but also helps to study the effect of nanomaterials on living objects, which is important for understanding and assessing the risks of using nanomaterials for both the environment and human health. The use of NM in biosensors and biofuel cells expands the views of the properties of NM and contributes to their study.

The main problem is the absence of links between scientific organizations, which develop laboratory models of bioelectrochemical devices, and businesses that could commercialize these models. For this reason, most developed models remain on the level of laboratory equipment, not finding practical implementation. It is hoped that this problem will be successfully solved in the future, and many efficient laboratory models will find their commercial application.

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Author contributions YVP, MR and ANR performed the content outline, literature collection, writing of paper and supervision and monitoring of the manuscript. All authors read and approved the final manuscript.

Declarations

Conflict of interest The authors declare that they have no conflict of interest in the publication.

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