

Modification of boron-doped diamond electrode and its applications

Oleksandr Matvieiev, Renáta Šelešovská*, and Lenka Janíková

*Institute of Environmental and Chemical Engineering,
The University of Pardubice, CZ–532 10 Pardubice, Czech Republic*

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Boron doped diamond (BDD) is a promising electrode material exhibiting exceptional electrochemical properties. Thanks to this, it is widely used in the field of electroanalytical chemistry. Simultaneously, BDDE is an excellent substrate for various surface modifications that allow the improvement of specific properties of electrodes, such as sensitivity and selectivity in particular. This article presents a comprehensive overview of the possibilities of modification of BDDEs. It summarizes the different types of modifications in the individual chapters devoted to modifications with metal and metal oxide nanoparticles, carbon materials, such as graphene or carbon nanotubes, and last but not least, organic molecules and biomolecules. It also deals with procedures and specific conditions for electrode modification. Finally, an overview of applications of modified BDDEs is also included.

Keywords: Voltammetry; Boron-doped diamond electrode; Modification; Application

Introduction

Boron-doped diamond electrodes (BDDEs) were introduced in the field of electroanalytical chemistry in the early 1990s [1–3]. BDDE was very promising electrode material due to the exceptional properties, such as wide usable potential window (up to 3 V), low background currents (low current noise), good chemical resistance (corrosion resistance even at anodic polarization), the resistance to passivation, high hardness, and thermal conductivity [4–7]. It is generally known that pure diamond is not an electrically conductive material, it is an insulator.

* Corresponding author, ✉ renata.selesovska@upce.cz

For its electrochemical use, it must be doped with atoms of other elements, most often, of boron. Depending on the concentration of these atoms, the electrochemical properties of the resulting electrode material may markedly differ [8]. The predominant use of boron is associated with a low charge carrier activation energy of 0.37 eV [9].

Diamond films are prepared by the so-called chemical vapor deposition (CVD), which uses hot fibers or microwave heating. A mixture of methane and hydrogen is used to deposit the film, and diborane is added to the mixture for the boron doping. The carrier is most often made of a silicon wafer, sometimes also being formed by molybdenum or tungsten [8].

As mentioned above, the concentration of boron in the diamond film has a great influence on the properties of BDDEs. It affects their morphology, quality, and electrochemical as well as spectral properties. Many studies on this topic have been published using Raman spectroscopy, scanning electron or atomic force microscopy, impedance spectroscopy, cyclic voltammetry of different redox markers, and other methods [10–14]. These studies have shown that BDD films deposited at a B/C ratio of 500–1000 ppm provide a semiconductor conductivity and at a ratio of 2000 and higher metallic conductivity. As the concentration of boron in the diamond film increases, the usable potential window decreases [10]. Generally, the electrochemical properties of the electrodes are improved with the increasing B/C ratio [11].

The process of pretreatment of the electrode surface before its use is no less important. A preliminary preparation can be most often accomplished by anodic or cathodic polarization, cyclic voltammetric polarization or polishing [15]. Anodic pretreatment is carried out at a potential of more than +2 V or at high current density, when the surface of the BDDE is enriched with oxygen atoms, which allows one to stabilize the surface properties of the electrode. After such preliminary preparation, the respective electrode is called O-terminated. In the case of cathodic pretreatment, polarization less than –2 V or high cathode current density is used. The surface of such electrode is enriched with hydrogen and being called H-terminated [16]. The use of cyclic voltammetry as a method of preliminary preparation of the electrode allows to stabilize its surface properties. Typically, such a treatment is carried out in a supporting electrolyte at a scan rate of 100 mV s⁻¹ and within a wide range of potentials from –(2–1) V to +(2–2.5) V [17,18]. Mechanical pretreatment by polishing differs significantly from anodic pretreatment. When being a polishing, the effect of surface charging or a change in valence band position for the anodized surface is observed. It leads to a higher speed of the anode processes. However, this type of pretreatment is not stable over time and the current density in the subsequent cycle is less than in the first one [15]. The cathodic treatment in comparison with the anodic ensures the higher conductivity. Hydroxyl radicals, enriching the surface after an anodic treatment are highly reactive and, consequently, the surface has a less good response because of incomplete inertness. On the other hand, the H-terminated

surface state is not stable. It is oxidized already in air, left alone when being measured in the area of positive potentials. Therefore, H-terminated surface must be formed repeatedly by incorporating a cathodic pretreatment prior to each scan [16]. Yet another possibility of the surface treatment of a BDDE is chemical (covalent) attachment of amino group or carboxyl group which can serve for example for immobilization of biomolecules (e.g., DNA, enzymes).

Due to its excellent properties, BDDEs have found wide application in electroanalytical chemistry. Moreover, in some cases, the use of this type of electrode can replace the mercury electrodes in voltammetric analysis, which leads to a more environmentally friendly procedures. A large number of articles have been published on the topic of determining a wide palette of substances using BDDE; e.g., drugs, pesticides, biomarkers of different diseases, environmental contaminants, carcinogenic and otherwise hazardous substances to health. Inorganic and organic substances as well as biomolecules could be determined. The published results were summarized in a series of review articles to date (see [15–24]). A promising application of BDDEs is in wastewater treatment, in particular, if being used as an anode material for the oxidation of organic pollutants [25,26].

The current demands on analytical methods involve untiring efforts to improve the selectivity and sensitivity of available techniques. The modification of commonly used working electrodes can be one of the perspective direction of a research in the area of electroanalytical chemistry. Modification techniques can be electrochemical, chemical, photochemical, or physical. The binding of organic functional groups or biomolecules and electrochemical deposition of metals or their oxides are the most commonly used procedures. Due to the biocompatibility of diamond, its use for *in vivo* sensors is advantageous. Therefore, BDDEs are also modified by various enzymes for medical and diagnostic applications [24]. As with other working electrodes, different types of carbon nanomaterials can also be used to modify BDDEs with the corresponding benefit.

Modification by metal and metal oxide nanoparticles

Modification of BDDE with metal nanoparticles (MNPs) is a simple tool to improve its electrochemical and electrocatalytic properties. It is most often realized by the process of electrochemical deposition from a solution of metal salts [27,28], by physical deposition [29,30] or implantation of ions [31,32]. Surface modification with nanoparticles brings a number of advantages. At first, these include a large active surface, which is related to the improvement of the catalytic activity, and increase in active sites in relation to the bare electrode. An increase in charge transfer rate can be achieved by modifying the surface of BDDE with redox active materials. The ratios of signal to noise are also increased,

diffusion enhances, and selectivity improves. Moreover, some analytes that are not observable at the bulk BDDE can be determined using modified electrodes; e.g., due to the reducing of activation overpotential [33].

The use of BDDEs modified with MNPs has been and still is of great interest and, so far, a number of reports have been published accordingly. In 2010, a review article by Toghil et al. summarized the available information on BDDEs modified with MNPs, its characterization and applications in electroanalytical chemistry published to date [33]. The following text will therefore be devoted to works dealing with analytical usage of BDDEs modified with MNPs published from 2010 to the present. Basic information from these publications, including a reference to the literature, is summarized in Table 1.

Electrodeposition of metal nanoparticles on the surface of a BDDE is a very simple process that does not require any special or expensive equipment. It can be applied to modify various substrates. In addition to the BDDE, electrodes made of different carbon materials were most often used [34,35]. Importantly, by controlling the deposition conditions, in particular the deposition potential and time, the metal concentration in the solution or the value of medium pH, a relatively reproducible surface modification can be obtained. In addition, it is possible to influence the size of the resulting nanoparticles, as well as the electrode coverage [27,28,33].

The ion implantation process is much more complicated and requires more demanding and sophisticated equipment compared to the electrodeposition. On the other hand, it provides more uniform and a very stable metal modification. Implantation is performed by exposing the surface of BDDE to metal ion bombardment from target metal ion source and the modified electrode is then annealed at high temperatures in the presence of hydrogen. This process allows the formation of metal nanoparticles on the surface of the BDD film [31–33]. The last and probably the simplest possibility is a wet chemical seeding, when the nanoparticles are prepared separately and then fixed on the electrode surface. MNPs are usually formed in a colloidal form in a solution where the electrode is immersed or the solution is applied onto the electrode surface, and allowed to dry [36–39].

Gold nanoparticles (AuNPs) are among the most commonly used nanomaterial for the modification of BDDEs [36–43]. For example, Kingkan et al. electrodeposited AuNPs on BDDE by dropping of 100 μL of a 0.1% w/w Au(III) solution in 1.0 mol L^{-1} HCl as supporting electrolyte upon the electrode surface, when the constant potential of -0.3 V vs. Ag/AgCl was set for a period of 60 s to reduce Au(III) to Au(0). The electrode prepared in this way was then applied to the determination of arsenic using square-wave anodic stripping voltammetry (SWASV). In this method, stable intermetallic of Au–As compounds could be formed during the deposition step, thus improving the effectiveness of the cathodic preconcentration of As(0) [40]. Other authors used chronoamperometry in solution of 1 mM $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ in 0.5mM H_2SO_4 at the potential of -0.2 V for electrolytic formation of AuNPs on the surface of BDDE. This electrode was used

for determination of antiviral drug *Zanamivir* [41]. Ivandini et al. modified BDD surface by immersion of the electrode treated with allylamine under UV irradiation in colloidal suspension of AuNPs for 20 min. This electrode served as biochemical oxygen demand sensor [37,44].

Copper nanoparticles (CuNPs) modified BDDEs are usually prepared by electrodeposition [45–49]. Jiwanti et al. performed electrodeposition from sulphate electrolytes at a constant potential of -0.6 V with different duration of the process from 50 to 300 s, when their modified electrode was used for electroreduction of CO_2 [45,49]. Electrodeposition of CuNPs can also be performed from an acetate electrolyte [47]. CuNPs, NiNPs as well as CuNiNPs can be used to modify the BDDE by both – wet chemical seeding and electrodeposition. A solution containing nickel nitrate and copper sulphate was used for electrodeposition. Wet chemical seeding was performed by dropping 100 μL of 1 M NaBH_4 in 0.1 M NaOH solution on the BDD surface and adding a metal precursor 1 mM $\text{Ni}(\text{NO}_3)_2$ or CuSO_4 [48].

Palladium belonging among precious metals is very often used as a catalyst for various reactions. Jiwanti et al. modified the surface of BDDE by palladium nanoparticles (PdNPs) by electrodeposition from the solution containing 1 mM PdCl_2 in 0.1 M HCl at a constant potential of -0.15 V. With the increasing electrodeposition time, the amount of palladium on the electrode surface increased too, which significantly affected the electrochemical properties of the electrode. This electrode was utilized for electroreduction of CO_2 [50]. The same authors prepared also tin-palladium nanoparticles (SnPdNPs) modified BDDEs, when the first step represented the electrodeposition of tin nanoparticles (SnNPs) from a solution of 0.26 M $\text{C}_2\text{H}_6\text{O}_6\text{S}_2\text{Sn}$ in 1 M $\text{CH}_3\text{SO}_3\text{H}$ by applying linear sweep voltammetric (LSV) ramp at potentials between -0.6 V and 0.0 V (*vs.* Ag/AgCl) at a scan rate of 0.01 V s^{-1} during one cycle. The electrodeposition of PdNPs was performed from the already known chloride electrolyte (1 mM PdCl_2 in solution of 0.1 M HCl). The so prepared modified BDDE was used for electrochemical oxidation of ethanol [51]. There is also an option to modify the BDDE with gold-palladium nanoparticles (AuPdNPs). The first step is a precipitation of AuNPs from an electrolyte containing hydrogen tetrachloroaurate (III) trihydrate and hydrochloric acid at 0.0 V (*vs.* Ag/AgCl). This is then followed by electrodeposition of PdNPs from the chloride electrolyte, but the concentration of palladium is twice lower than in previous methods, and the electrodeposition potential is set to -0.20 V (*vs.* Ag/AgCl). This BDDE modified with AuPdNPs was applied to the reduction of oxygen [52].

As for most of the mentioned metals, electrodeposition from acidic media was usually used also to modify BDDE with platinum nanoparticles (PtNPs). Figueiredo-Filho et al. used a solution containing 1.0 mM PtCl_4 in 0.1 M HCl solution at a constant potential of -0.94 V (*vs.* Ag/AgCl). This modified BDDE was used for determination of herbicide *Linuron* [53]. Hernández-Lebrón and Cabrera electroplated PtNPs from solution of 1 mM platinum in 0.5 M H_2SO_4

under the cycling in potential range between -0.2 V and $+1.0$ V (vs. Ag/AgCl) at scan rate of 100 mV s⁻¹. This electrode was applied to enhance the ammonia oxidation [54]. Other authors used a BDDE modified with PtNPs to determine of neuraminidase based on zanamivir inhibition reaction [55] and for electrochemical conversion of CO₂ [49].

Iridium is yet another precious metal used for modifying. In the respective report [56], the authors propose a modification of BDDE with iridium nanoparticles (IrNPs) in three steps: wet chemical seeding, electrodeposition, and another electrodeposition after rapid thermal annealing. A fairly stable iridium-modified BDDE was utilized for electrochemical determination of arsenic(III). Dewandaru et al. performed electrodeposition in a solution of 1 mM K₂IrCl₆ in 0.5 M H₂SO₄ at a potential of $+0.06$ V (vs. Ag/AgCl). They applied this electrode to perform the electroreduction of CO₂ [49,57]. Atriardi et al. described several methods for obtaining platinum-iridium nanoparticles (PtIrNPs) for modification of BDDE. In the first case, the hydrothermal method was used: 1 mM H₂PtCl₆ and 1 mM K₂IrCl₆ were mixed and boiled under stirring until the volume of the mixture was reduced. Then, the mixture was transferred to an autoclave containing formaldehyde and heated at 180 °C for 10 h. Separately, a BDDE was converted into an N-terminated electrode by the addition of allylamine to the BDD surface under illumination with a UV lamp. Pt-Ir modified BDD was prepared by the immersion of the N-terminated BDD into a Pt-IrNPs solution for 12 h. In the second method, chemical deposition of PtIrNPs followed by electrochemical build-up was used [58].

Electrodeposition of silver nanoparticles (AgNPs) was performed from a solution containing 0.1 ml of nafion (5 wt.%) and 10 ml of 1 mM silver nitrate with stirring at a constant potential of $+1.0$ V. This electrode can be used for electrocarboxylation of benzophenone [59]. Other authors applied similarly modified electrode for determination of cholesterol [60].

Nickel nanoparticles (NiNPs) can be electrodeposited from electrolyte of 0.1 M NaH₂PO₄ [61] as well as from acetate buffer solution (pH 5) [62,63]. Ni(NO₃)₂ or NiSO₄·6H₂O served as a source of nickel. These modified electrodes were used for electroanalysis of L-alanine [61] and as an electrode material in fuel cells [62,63]. NiNPs can also be obtained by physical methods. The Ni layer was sputtered from the Ni target by direct-current magnetron in argon atmosphere. The so prepared electrode was used for non-enzymatic determination of glucose [64]. Cobalt nanoparticles (CoNPs) are also used to modify BDDE. CoNPs can be obtained from an electrolyte containing CoCl₂·6H₂O dissolved in acetate buffer solution at potential of -1.0 V. Nickel-cobalt nanoparticles (NiCoNPs) can then be obtained from an electrolyte containing nickel sulphate and cobalt chloride in acetate buffer solution at a constant potential of -1.2 V. BDDEs modified with CoNPs and NiCoNPs have also been used as electrode materials in fuel cells [63].

Table 1 Modification of BDDE by metal nanoparticles and their application

Type nanoparticle	Modification procedure	Application	Reference
Au	Electrodeposition (electrolyte – HCl; metal source – AuCl ₃ ; potential value –0.3 V)	arsenic (III)	[40]
Au	Electrodeposition (H ₂ SO ₄ ; HAuCl ₄ ; –0.2 V)	neuraminidase	[41]
Au	Electrodeposition (H ₂ SO ₄ ; HAuCl ₄ ; –0.7 V)	small organic molecules	[42]
Au	Ion sputtering technology	clenbuterol	[43]
Au	Physical deposition – AuNPs suspension, drying in nitrogen atmosphere	catechol	[36]
Au	Physical deposition – allylamine treatment under UV irradiation, AuNPs suspension	biochemical oxygen demand sensor	[41]
Au	Electrodeposition (H ₂ SO ₄ ; HAuCl ₄ ; +0.0 V)	oxygen	[52]
Au	Physical deposition – allylamine treatment under UV irradiation, AuNPs suspension	biochemical oxygen demand sensor	[37]
Au	Physical deposition – allylamine treatment under UV irradiation, AuNPs suspension	biochemical oxygen demand sensor	[44]
Au	Layer-by-layer self-assembly technique	electrode material microbial fuel cells	[66]
Au-Pd	Physical deposition – Au-PdNP suspension	oxygen	[38]
Au-Cu	Physical deposition – Au-CuNPs suspension	oxygen	[39]
Au-C-Ni	Alternate application of layers using direct current (DS) sputtering	dopamine	[67]
Cu	Electrodeposition (H ₂ SO ₄ ; CuSO ₄ ; –0.6 V)	reduction of CO ₂	[45]
Cu	Electrodeposition (AcBS (pH 5.6); (CH ₃ COO) ₂ Cu; –0.8 V)	reduction of CO ₂	[47]
Cu-Ni	Electrodeposition (H ₂ SO ₄ ; NiSO ₄ , CuSO ₄ ; –1.2 V)	reduction of CO ₂	[48]
Cu	Electrodeposition (H ₂ SO ₄ ; CuSO ₄ ; –0.2 V)	reduction of CO ₂	[49]
Pd	Electrodeposition (HCl, PdCl ₂ ; –0.15 V)	reduction of CO ₂	[50]
Pd	Electrodeposition (HCl; PdCl ₂ ; –0.15 V)	ethanol	[51]
Pd-Sn	Electrodeposition (step 1: HCl; PdCl ₂ ; –0.15 V; step 2: CH ₃ SO ₃ H; C ₂ H ₆ O ₆ S ₂ Sn; CV: –0.6 to +0.0 V)	ethanol	[51]
Pd	Electrodeposition (HCl; PdCl ₂ ; –0.12 V)	oxygen	[52]
Pt	Electrodeposition (H ₂ SO ₄ ; H ₂ PtCl ₆ ; –0.2 V)	reduction of CO ₂	[49]
Pt	Electrodeposition (H ₂ SO ₄ ; K ₂ PtCl ₆ ; CV: –0.2 to +1.0 V)	ammonia	[54]
Pt	Electrodeposition (H ₂ SO ₄ ; H ₂ PtCl ₆ ; –0.2 V)	neuraminidase	[55]
Pt	Electrodeposition (HCl; PtCl ₄ ; –0.94 V)	linuron	[53]
Ir	Electrodeposition (H ₂ SO ₄ ; H ₂ IrCl ₆ ; +0.6 V)	reduction of CO ₂	[49]
Ir	Electrodeposition (H ₃ PO ₄ ; K ₂ IrCl ₆ ; +0.6 V)	arsenic (III)	[56]
Ir	Electrodeposition (H ₂ SO ₄ ; K ₂ IrCl ₆ ; +0.6 V)	reduction of CO ₂	[57]
Pt-Ir	A hydrothermal method with electrochemical build-up; Electrodeposition (H ₂ SO ₄ ; H ₂ PtCl ₆ , K ₂ IrCl ₆ ; –0.5 V)	reduction of CO ₂	[58]

Table 1 Modification of BDDE by metal nanoparticles and their application (continued)

Type nanoparticle	Modification procedure	Application	Reference
Ag	Electrodeposition (Nafion; AgNO ₃ ; +1.0 V)	electrocarboxylation of benzophenone	[59]
Ag	Electrodeposition (BRB (pH 2); AgNO ₃ ; -0.5 V)	cholesterol	[60]
Ni	Electrodeposition (NaH ₂ PO ₄ ; Ni(NO ₃) ₂ ; CV: -0.6 to +0.6 V)	L-alanine	[61]
Ni	Electrodeposition (AcBS (pH 5); Ni(NO ₃) ₂ ; -1.3 V)	electrode material in fuel cells	[62]
Ni	Electrodeposition (AcBS (pH 5); Ni(NO ₃) ₂ ; -1.2 V)	electrode materials in fuel cells	[63]
Ni	Vacuum spraying	glucose	[64]
Co	Electrodeposition (AcBS (pH 5); CoCl ₂ ; -1.0 V)	electrode materials in fuel cells	[63]
Ni-Co	Electrodeposition (AcBS (pH 5); Ni(NO ₃) ₂ , CoCl ₂ ; -1.2 V)	electrode materials in fuel cells	[63]
Bi	Electrodeposition <i>in situ</i> during analyte accumulation (Bi(NO ₃) ₃)	heavy metals	[65]
Bi	Electrodeposition (HClO ₄ (pH 1.2); Bi(NO ₃) ₃ ; -1.0 V)	heavy metals	[27]
Bi	Electrodeposition <i>in situ</i> during analyte accumulation (Bi (III))	cadmium	[68]
Bi	Electrodeposition <i>in situ</i> during analyte accumulation (Bi (III))	heavy metals	[69]

Abbreviations: AcBS – acetate buffer solution, BRB – Britton-Robinson buffer, CV – cyclic voltammetry

Bismuth nanoparticles (BiNPs) modified BDDEs, as an alternative to mercury electrodes, were prepared by electrodeposition from solution of Bi(III) salt. Electrodeposition was carried out at a potential of -1.2 V, after a while the potential was changed by +0.3 V. Bismuth modified BDDEs are usually used to determine heavy metals [27,65].

An overview of the modifications of BDDEs by metal oxide nanoparticles (MONPs) described in the literature is given in Table 2. The first mention of modifying the BDDE with MONPs was published in 2001 [70]. The authors investigated the electrocatalytic properties of ruthenium and iridium oxide as a catalyst for the electroreduction of chlorine. The main advantage of MONPs is greater stability compared to MNPs. While the metal nanoparticles can dissolve into the solution in the form of ions during some anodic processes, MONPs are more stable [70]. Iridium oxide (IrO₂NPs) has been proven to be a good catalyst in electrochemical reactions. Modification can be carried out for example from an alkaline solution containing 0.5 mM Na₂IrCl₆ dissolved in 0.1 M KNO₃. The emerging Ir₂O₃·xH₂O is then electrochemically deposited on the electrode surface during cyclic voltammetry in a potential range from +0.2 V to +1.2 V. This

electrode was applied to electrochemical reduction of CO₂ [71] and for the determination of arsenic(III) [72]. Salimi et al. applied BDDE modified with IrO₂NPs for amperometric determination of mercury(I) [73]. Iridium oxide (as well as ruthenium oxide) can be obtained by the sol-gel method. The oxides are obtained in a solution (or in the form of a paste) which is applied onto the surface of the electrode, which is then subjected to heat treatment. The resultant electrode was used as electrocatalysts for chlorine oxidation [70]. The production of ruthenium oxide (RuO₂NPs) nanoparticles has been well described by McKenzie et al. RuO₂NPs were obtained in a colloidal solution with subsequent adsorption on the BDDE due to electrostatic interaction. Such an electrode can be used in anode electrosynthesis [74]. RuO₂NPs can also be applied by thermal decomposition of an alcoholic solution of ruthenium chloride. This procedure should be repeated several times to increase the amount of ruthenium on the surface of the BDDE. This way modified electrode was used in the electrochemical reduction of CO₂ [75].

Obtaining copper oxide nanoparticles (CuO₂NPs) for modification of BDDEs can be carried out from acetate electrolyte using a constant potential of +1 V or a short pulses of potential +1 V. A pulse method of electrodeposition of CuO₂ leads to more uniform NPs [76]. Other authors obtained copper oxide at a potential of -0.43 V and applied this electrode also in the electrochemical reduction of CO₂ [47,77]. The Mavrokefalos et al. proposed to obtain CuO₂NPs from an electrolyte of 1.5 M lactic acid and 1.9 M NaOH containing 0.2 M CuSO₄·5H₂O at a direct current of -6.6 mA. Such an electrode was used as an efficient photocathode for solar hydrogen generation [78].

Zinc oxide nanoparticles (ZnONPs) on BDDE surface were obtained by a complex method. First, a layer of nickel was applied onto the BDDE by the physical method. Subsequently, the nickel was etched to create a porous surface. The first layer of ZnO was applied by hydrothermal method when the electrode was then annealed at a high temperature to form an oxide. The increasing of the ZnO layer was ensured also by hydrothermal method. Such an electrode was utilized for the photoelectrocatalytic oxidation of aniline [79].

Titanium (IV) oxide (TiO₂NPs) for modification of the BDDE was obtained by electrodeposition from a solution containing 50 mM TiCl₃ in the supporting electrolyte of pH 2 at a constant potential. By this way modified electrode had good electrocatalytic properties for the oxidation of ethyl alcohol and therefore it can be used to create fuel cells [80].

Braiek et al. proposed the following modification of the BDDE. Carboxyl magnetic particles of Fe₃O₄ were first activated in a solution containing 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide and *N*-hydroxysuccinimide. After activation, the particles were washed with water and then mixed with gold nanoparticles. As a result, they obtained a solution containing metal oxide particles ended by gold nanoparticles. This composite was applied to the electrode surface and dried. This modification was used for detection of a cancer biomarker interleukin-8 [81].

Table 2 Modification of BDDE by metal oxide nanoparticles and their application

Type nanoparticle	Modification procedure	Application	Reference
IrO ₂	Electrodeposition (electrolyte – KNO ₃ ; oxide source – Na ₂ IrCl ₆ ; CV +0.2 to +1.2 V)	reduction of CO ₂	[71]
IrO ₂	Electrodeposition (HCl; K ₃ IrCl ₆ ; CV –0.2 to +1.2 V)	arsenic (III)	[72]
IrO ₂	Electrodeposition (PBS (pH 10.5); K ₃ IrCl ₆ ; CV –0.2 to +1.2 V)	reduction of CO ₂	[73]
IrO ₂ RuO ₂	Sol-gel method	chlorine reduction	[70]
RuO ₂	Sol-gel method	anode electrosynthesis	[74]
RuO ₂	Thermal decomposition of an alcoholic solution of RuCl ₃	reduction of CO ₂	[75]
CuO CuO-Cu	Electrodeposition (AcBS (pH 5.6); (CH ₃ COO) ₂ Cu; –0.43 V)	reduction of CO ₂	[47]
Cu ₂ O	Electrodeposition (AcBS (pH 5.6); (CH ₃ COO) ₂ Cu; –1 V)	–	[76]
Cu ₂ O	Electrodeposition (AcBS (pH 5.6); (CH ₃ COO) ₂ Cu; –1.0 V)	reduction of CO ₂	[77]
Cu ₂ O	Electrodeposition (Lactic acid, NaOH; CuSO ₄ ; –6.6 mA)	photocathode for solar hydrogen generation	[78]
ZnO	Hydrothermal method	oxidation of aniline	[79]
TiO ₂	Electrodeposition (HCl, TiCl ₃ ; 0.0 V)	catalytic material for fuel cells	[80]
Fe ₃ O ₄ -Au	Physical deposition – Fe ₃ O ₄ -Au suspension, drying in nitrogen atmosphere	cancer biomarker interleukin-8	[81]

Abbreviation: AcBS – acetate buffer solution, PBS – phosphate buffer solution

Modification by organic molecules and biomolecules

Another way to modify the surface of BDDEs is to attach various organic molecules and biomolecules to their surface. There are many ways to obtain such modified electrodes. For example, it is possible to incorporate a suitable modifier into the polymer film covering the electrode. Covalent (chemical) attachment of the modifier to the electrode surface is also possible. In this case, it is important to select an appropriate functional group of the modifier applied. Another option is the physical adsorption or spontaneous chemisorption of the modifier.

Adsorption of electroactive substances on the electrode surface is a simple method of surface modification. It represents an equilibrium-controlled process. The modifier is often weakly bound to the electrode surface, which usually leads to desorption in a relatively short time. In chemisorption, valence forces of similar kind as those acting in the formation of chemical compounds are involved. The resulting chemical film is then strongly and almost ideally irreversibly adsorbed (chemisorbed) onto the electrode surface. There is usually a monolayer (or less)

of coverage. This type of modification includes also the self-assembled monolayers (SAMs), in which uncorrelated molecules spontaneously chemisorb at specific sites onto the electrode surface to form a super-lattice [82]. Yet stronger attachment to the electrode surface can be accomplished by covalent linking of the desired component to surface groups present at or formed directly on the substrate. Such covalent linking procedures frequently employ organo-silanes and other linking agents. The substrate surface is usually pretreated; e.g., by an oxidative reaction, forming the required surface groups. The surface is then treated with the linking agent and the desired component [83]. By using polymeric modifying layers, fairly thick films, containing much more electroactive sites than a monolayer, can be formed on an electrode surface. Various types of polymers can be prepared on the surface of the electrodes, e.g., electroactive polymers containing oxidizable or reducible groups covalently linked to the polymer back-bone, coordinating polymers containing groups that can coordinate to the species like metal ions and bring them into the polymer matrix, ion-exchange polymers containing charged sites that can bind ions from solution via an ion-exchange process, biological polymers (enzymes or proteins) utilized for biosensors application, etc. [83]. Selected examples of modification of BDDEs by organic molecules and biomolecules are given below and a survey of the respective applications then gathered in Table 3.

In 2014, BDDE covered with Nafion[®] and lead film (PbF/Nafion/BDDE) was firstly applied to the simultaneous determination of *Paracetamol* (PA) and ascorbic acid (AA) [84]. The main advantage of this electrode was that the sensitivity increased and the separation of signals of both analytes had been improved due to the lead layer formed. For the preparation of modified electrode, one drop of 1% Nafion solution was placed on the BDD surface and left to dry in air. Then, the lead-film coating and voltammetric determinations of PA and AA were carried out in a solution containing 0.1 M ammonia buffer (pH 8.3), 0.02 M potassium sodium tartrate, $1 \cdot 10^{-5}$ M $\text{Pb}(\text{NO}_3)_2$ and the varied concentrations of analytes. At the potential of -1.55 V vs. ref., the lead film was plated onto the Nafion covered BDDE [84]. The same authors later applied this electrode also to the simultaneous determination of PA and dopamine (DA) [85]. Rusinek et al. [86] pipetted the solution of Nafion onto the BDD surface prior to spin-coating. By changing the polymer concentration and spin rate, they were able to control the polymer film thickness. This electrode was used as spectroelectrochemical sensor for the determination of 4-aminophenol and hydroquinone. Buzid et al. performed the electrode modification by applying a solution of Nafion (2 % (w/v), in ethanol) onto the polished BDD surface followed by the drying in vacuum. This electrode was used to determine biotin [87]. Other authors applied Nafion-modified BDDE for simultaneous analysis of guaiacol and its analogs [88], and for determination of caffeine [89] or dopamine [90]. The modification of the BDDE with cellulose is similarly simple as in case of Nafion and the resulting surface can be also used

to generate thin sensor films. Bonn e et al. modified the polished electrode in a solution containing 1.5 M NaOH with 0.65 M thiourea and 3 wt. % cellulose using potential cycles between -0.1 V and 0.5 V vs. SCE [91].

The surface of the BDDE can also be modified by electropolymerization, when the modifier can e.g. be poly-L-arginine, poly-L-lysine, or polyaniline. Poly-L-lysine-modified BDDE can be obtained in two ways. The wet chemical modification was the first step when the electrode had been immersed in solution consisting of 0.1 % poly-L-lysine dissolved in 5 ml of water for 24 h. Then, the modified electrode was removed from the solution, washed, and dried under the nitrogen atmosphere. The electro-polymerization was performed in phosphate buffer solution (pH 7.4) by CV at a potential range from $+0.5$ to $+1.5$ V (vs. Ag/AgCl) with a scan rate of 100 mV s⁻¹ for 30 cycles. The prepared electrode was applied to determine adenine and guanine [92]. Next modifier, poly-L-arginine was electrodeposited by CV in the potential range from -1.1 to $+2.5$ V at 100 mVs⁻¹ for 10 cycles. Poly-L-arginine modified BDDE was applied to the determination of terbutaline sulphate [93]. In addition, conductive polymers can also be used to prepare DNA hybridization sensors. Gu et al. studied the immobilization of DNA on BDDE modified by thin layer of polyaniline-poly(acrylic acid) composite polymer film. The carboxylic acid residues in the polymer film act as the binding sites for the attachment of DNA, whilst the conductive polymer matrix enhances the electron-transfer between DNA and the diamond surface [94]. Polyaniline-poly(vinyl sulfonate) modified BDDE was prepared by electropolymerization performed in a solution containing sulfuric acid, aniline, and polyvinyl alcohol also by cycling between potentials of -200 and $+1200$ mV at 50 mV s⁻¹ (vs. Ag/AgCl) for 10 cycles. The BDDE with this modification was used as a tyrosinase biosensor [95]. A monomer in solution of 0.5 M Na₂SO₄ and 0.1 M H₂SO₄ (pH 1) was applied for the preparation of BDDE modified with Poly(*N,N*-dimethylaniline) used to determine ascorbic acid and serotonin [96].

The authors in paper [97] proposed two ways to modify the BDDE by polymers. Electropolymerization was performed in a solution of 0.1 M *N*-acetyltyramine and 10 mM sulfobutylether- β -cyclodextrin dissolved in 0.3 M NaOH by cycling between -0.1 V and $+1.7$ V (vs. Ag/AgCl) at 500 mV s⁻¹ for 40 cycles. The electrode prepared in this way can additionally be electrocolarized by pyrrole (50 mM pyrrole in 50 mM phosphate buffer, pH 7.0) by cycling in the potential range -0.1 V and $+1$ V (vs. Ag/AgCl) at 50 mV s⁻¹ for 10 cycles. These modifications of the BDDE were used to determine dopamine [97]. The same authors [98] proposed a similar modification when electro-polymerization was performed in a solution of 0.1 M tyramine hydrochloride in methanol containing 0.3 M NaOH by cycling (-0.1 V and $+1.7$ V (vs. Ag/AgCl)) at 500 mV s⁻¹. The next step was the electro-polymerization in solution of 50 mM pyrrole-1-propionic acid in phosphate buffer (pH 7.0) by cycling (-0.1 V and $+1.1$ V (vs. Ag/AgCl)). This electrode was also used to determine dopamine [98]. Modification of the BDDE only by polypyrrole was carried out using CV. The electrode was subjected

to a solution containing 0.1 M NaClO₄ and 50 mM pyrrole applying the range of potentials from -0.5 to 0.75 V at 100 mV s⁻¹. The final step was peroxidation in a solution of 0.5 M NaOH in the potential range from 0.0 to $+1.1$ V. The electrode was used to determine *Methylparaben* [99].

Application of a composite material is another possibility how to modify BDDE. In literature, modification with Polyaniline-Au [100] or Pt-tyramine [101] was described. In the first case, polymer was applied onto the electrode surface by electropolymerization from a solution containing 0.1 M aniline in 0.2 M H₂SO₄ at a constant potential of $+1.5$ V for 720 s. The electrode was washed, dried, and subjected to over-oxidation by amperometry ($+0.8$ V for 600 s) in 0.5 M H₂SO₄. The final stage of modification was the application of gold nanoparticles from a solution containing 2.0 mM HAuCl₄ in 0.5 M H₂SO₄ under a constant potential of -0.5 V for 600 s. The modified electrode was used for the determination of dopamine [100]. Song et al. applied a similar procedure in two steps modified the BDDE by Pt-polyaniline. This modification was used to determine glucose [102]. Pt-Tyramine modified BDDE was prepared also in two steps. Electrodeposition of PtNPs was realized from sulphate electrolyte. The electropolymerization was performed from a solution containing 0.1 M tyramine hydrochloride in 50mM phosphate buffer (pH 7) and 10 mM sulphobutylether- β -cyclodextrin. The electrode was applied as a glucose biosensor [101]. There is also a method for modifying the BDDE by electrodeposition of PtNPs and in the next step by adsorption of hemoglobin. This Pt-hemoglobin modified BDDE was used for electrochemical determination of acrylamide [103]. An interesting method of BDDE modification was described by Kondo et al. The electrode was first photochemically modified with 4-vinylpyridine and then immersed in a solution containing cobalt (II) phthalocyanine. The obtained cobalt-phthalocyanine-BDDE was used to determine hydrogen peroxide [104].

Modification of the BDDE with hemoglobin alone was carried out by immersion of the electrode in a solution containing of 4 g L⁻¹ hemoglobin for 4 hours. This electrode was successfully used for the synthesis of silver nanoparticles in solution because hemoglobin on the surface of the BDDE prevents electrodeposition of silver, and promotes the electroreduction of silver ions remaining in solution in the form of colloidal particles [105]. Svítková et al. proposed modification of the BBD electrode by guanosine monophosphate. Its solution was applied to the electrode surface and dried. This electrode was utilized for the determination of pesticide *Alachlor* [106].

A separate chapter in the area of surface modification of the BDDE is the use of biomolecules, more specifically, the modification by enzymes or DNA. Biomolecules can be covalently bound on an electrode surface. It was found that organic functional groups, such as amino groups and carboxyl groups, introduced by covalent modification can serve to immobilize biomolecules, including DNA and enzymes, onto the diamond surface [23]. The most common enzyme for the preparation of biosensors based on modified BDDEs is glucose oxidase (GOx).

Wang et al. [107] attached the GOx to the surface of ultranano-crystalline diamond films via the tethered aminophenyl functional groups which had previously been grafted to the electrode surface by electrochemical reduction of an aryl diazonium salt. The authors demonstrated the functionality of the proposed biosensor in the detection of glucose via the direct anodic oxidation of H₂O₂. In recent years, a number of authors have described the development of biosensors based on the BDDE modified with GOx for the determination of glucose [108–111]. Another enzyme used to prepare biosensors is tyrosinase which was immobilized on amine-terminated BDD surface. These systems were applied in the detection of phenolic compounds [112–114].

Due to the inert nature of diamond surfaces, the immobilization of DNA and other proteins on diamond for the preparation of biosensors requires surface activation process. Yang et al. [115] applied photochemical methods to introduce a homogeneous layer of amine group on diamond serving as binding sites for DNA attachment. It was proved that the DNA-modified diamond substrates were highly selective and stable in the subsequent hybridization processes [115–117]. DNA-modified BDDEs were utilized also for detection of DNA cleavage [118]. Svitkova et al. [119] applied DNA-modified BDDE as a simple electrochemical platform for studying the damage to DNA by antihypertensive amlodipine. In this case, two ways of DNA immobilization, such as simple drop-casting approach and potentiostatic accumulation (+0.3 V, 10 min) were investigated. Wu et al. [120] described strong electrocatalytic effect of pyrrole-DNA-modified BDDE upon the redox reaction of clenbuterol. This principle was used for a determination in a sample of pig liver.

Table 3 Modification of BDDE by organic molecules and biomolecules and their application

Type polymer	Modification procedure	Application	Reference
Nafion-Pb	Drying of the solution on the electrode surface	paracetamol and ascorbic acid	[84]
Nafion-Pb	Drying of the solution on the electrode surface	paracetamol and dopamine	[85]
Nafion	Drying of the solution on the electrode surface	4-aminophenol and hydroquinone	[86]
Nafion	Drying of the solution on the electrode surface	biotin	[87]
Nafion	Drying of the solution on the electrode surface	guaiacol and analogs	[88]
Nafion	Drying of the solution on the electrode surface	caffeine	[89]
Nafion	Drying of the solution on the electrode surface	dopamine	[90]

Table 3 Modification of BDDE by organic molecules and biomolecules and their application (continued)

Type polymer	Modification procedure	Application	Reference
Cellulose	Electrodeposition (electrolyte – NaOH, thiourea; polymer source – cellulose; CV: –0.1 to +0.5 V)	generate thin sensor films	[91]
Poly-L-lysine	Chemical and electrochemical polymerization by CV in the potential range of +0.5 V to +1.5 V	guanine and adenine	[92]
Poly-L-arginine	Electrochemical polymerization by CV in the potential range of –1.1 V to +2.5 V	terbutaline sulphate	[93]
PANI-poly(acrylic acid)	Electrochemical polymerization by CV in the potential range of –0.2 V to +1.2 V	DNA hybridization analysis	[94]
PANI-poly(vinyl sulphonate)	Electrochemical polymerization by CV in the potential range of –0.2 V to +1.2 V	tyrosinase biosensor	[95]
Poly(DMA)	Electrochemical polymerization by CV in the potential range of –0.2 V to +1.5 V	ascorbic acid and serotonin	[96]
SBCPAC and PPCF	Electrochemical polymerization by CV in the potential range	dopamine	[97]
Poly-Ty and poly-PPA	Electrochemical polymerization by CV in the potential range	dopamine	[98]
Polypyrrole	Electrochemical polymerization by CV in the potential range of –0.5 V to +0.75 V	methylparaben	[99]
PANI-Au	Electrochemical polymerization Polyaniline and next electrochemically deposited AuNPs	dopamine	[100]
Pt-Ty	Electrodeposition PtNPs and electrochemical polymerization Tyramine	glucose	[101]
Pt-PANI	Electrodeposition PtNPs and electrochemical polymerization Polyaniline	glucose	[102]
Pt-Hemoglobin	Electrodeposition PtNPs and adsorbed hemoglobin	acrylamide	[103]
Co-Phthalocyanine	Photochemical modification	hydrogen peroxide	[104]
Hemoglobin	Physical adsorption in hemoglobin solution	synthesis of AgNPs	[105]
Guanosine monophosphate	Drying of the solution on the electrode surface	pesticide alachlor	[106]
GOx	The electrode surface grafted by aminophenyl functional groups was immersed in a solution of glucose oxidase and incubated	glucose	[107]
GOx	The enzyme solution is applied to the surface of the electrode and induced	glucose	[108]
GOx	The enzyme solution is applied to the surface of the electrode for 20 min	glucose	[109]

Table 3 Modification of BDDE by organic molecules and biomolecules and their application (continued)

Type polymer	Modification procedure	Application	Reference
GOx	The surface was photochemically modified with 4-vinylpyridine, cobalt phthalocyanine was subsequently attached. Electrochemical polymerization of GOx by CV in the potential range of +0.0 V to +0.6 V	glucose	[110]
GOx	Drying of the solution on the electrode surface	glucose	[111]
Tyrosinase	Drying of the solution on the electrode surface and incubation	phenolic compounds	[112]
Tyrosinase	A tyrosinase solution was applied to the phenolically functionalized BDD surface and incubated	phenolic compounds	[113]
Tyrosinase	Physical adsorption in solution	phenolic compounds	[114]
DNA	DNA is attached to photochemically modified BDD electrode	hybridization sensor	[115]
DNA	DNA is attached to photochemically modified BDD electrode	hybridization sensor	[116]
DNA	DNA is attached to photochemically modified BDD electrode	hybridization sensor	[117]
DNA	Maleimide terminated surface is incubated in solution to fixing DNA on the BDDE	DNA cleavage	[118]
DNA	1: drying of the DNA solution on the electrode surface 2: electrochemical polymerization by CV in potential range +0.1 V to +0.9 V	damage to DNA by antihypertensive amlodipine	[119]
Pyrrole-DNA	–	clenbuterol	[120]
Ruthenium tris(2,2')bipyridyl	Electrochemical polymerization by CV in the potential range of –1 V to +1 V	vitamin B ₆	[121]
PMo ₁₂ -ATAB-BDDE	Photochemical method	–	[122]

Abbreviations: ATAB – allyltriethylammonium bromide, DMA – *N,N*-dimethylaniline, GOx – glucose oxidase, PANI – polyaniline, PMo₁₂ – phosphomolybdic acid, PPA – pyrrole-1-propionic acid, PPCF – polypyrrole composite film, SBCPAC – sulfobutylether- β -cyclodextrin-doped poly(*N*-acetyltyramine), Ty – tyramine

Modification by carbon materials

Usually, the BDDE has a conductivity sp^3 , but by modifying it with carbon compounds it is possible to obtain a combined conductivity of sp^2 and sp^3 . Such modifying agents usually include various allotropic modifications of carbon; concretely, graphene, carbon nanotubes, and different carbon materials [123,124].

Carbon materials exhibit outstanding features as a high surface area, high electrical conductivity, electron mobility at a room temperature, flexibility, and a mechanical resistance, making them particularly attractive in the sensors field. An overview on the modifications of BDDEs by carbon materials described in the literature is surveyed in Table 4.

The application of the suspension of carbon nano-materials to the BDD surface represents the simplest modification method. This procedure was used e.g., for preparation of nano-carbon black modified BDDE when a suspension of carbon black in chloroform was applied to the electrode surface and allowed to dry. This modified electrode was used for electrochemical determination of chlorogenic acid [123]. Another widely used material in electrochemistry is graphene. It is a good choice for constructing the recognition layer of the sensor due to its unique morphological characteristics, chemical stability, and high electrical conductivity. The large surface area in connection with the excellent electrochemical properties of graphene could improve the transfer electron rate and the detection sensitivity [124]. Modification by graphene can be carried out by electrochemical deposition from a solution containing graphene oxide (4 mg mL^{-1}) in acetate buffer (pH 5.6) at a constant potential of -1.2 V (vs. SCE). The obtained electrode was utilized for the simultaneous detection of *Carbaryl* and *Paraquat* pesticides [125]. Pei et al. modified the surface of the BDDE with graphene in a slightly more complicated way. Initially, a copper film was deposited to the BDD surface using magnetron sputtering. Cu-graphene-BDD structure was prepared through vacuum annealing. Next, the Cu-film on the surface after annealing was etched to prepare the G/BDD configuration. This electrode was used to detect lead ions in seawater [126].

In addition to the graphene itself, a composite material consisting of graphene and silver nanoparticles was also used to modify the BDDE. Silver (and metals in general) introduces electrocatalytic activity into the system, which is reflected in a higher electron transfer rate. Graphene was electrodeposited as it was mentioned above at the potential of -1.2 V (vs. SCE) from a solution of graphene oxide (4 mg/mL) in 0.1 M KClO_4 supporting electrolyte. It follows the electrodeposition of AgNPs at -1.2 V (vs. SCE) from the solution of 10 mM AgNO_3 . The electrode prepared in this way was used to determine pesticides *Carbaryl* and *Paraquat* pesticides [127]. Another composite consisting of AuNPs and carbon spheres (CSs) was applied to prepare biosensor for determination of organophosphate pesticides. First, the nanocomposite was prepared, then, solutions of HAuCl_4 and K_2CO_3 added to the water-dispersed CSs. The freshly prepared NaBH_4 solution was subsequently added until the color turned to red. The resulting AuNPs-coated CSs were washed several times with distilled water, and a solution of HAuCl_4 and $\text{NH}_2\text{OH}\cdot\text{HCl}$ added again to increase and stabilize the amount of AuNPs grown on the CSs surface. The obtained solution was applied onto the BDDE surface and dried. AuNPs-CSs-BDDE was used to fabrication of acetylcholinesterase biosensor by application of acetylcholinesterase solution to the surface and incubation

at room temperature [128]. The chitosan-carbon nanotubes (chitosan-CNT) modified BDDE decorated with AuNPs can be another example. Modification was created using suspension containing chitosan, CNTs, and AuNPS which was applied onto the electrode surface and allowed to dry. The resultant electrode was used to determine catechol [36]. Long et al. described nickel-encapsulated carbon nanotubes modified BDDE for non-enzymatic glucose sensing. In this case, Ni film was deposited on the BDD film under the nitrogen atmosphere by DC magnetron sputtering. Subsequently, carbon nanotubes were grown via chemical vapour deposition [129].

The multiwalled carbon nanotubes (MWCNTs) have been extensively used to modify electrodes especially due to a very high surface area. When modifying BDDEs, they are usually applied together with other substances, such as Nafion, enzymes, etc. Gayen et al. introduced MWCNTs-Nafion modified BDDE. An appropriate volume of a suspension of MWCNTs in the Nafion solution was pipetted onto the electrode surface and allowed to dry. A stable coating was achieved by dropping another solution of Nafion and KH_2PO_4 mixture (without MWCNT) onto the modified electrode dried under air. This electrode was used for determination of antibiotic *Ciprofloxacin* [130]. MWCNTs-Tyrosinase modified BDDE was developed by Zehani et al. for determination of bisphenol A. Modification of the BDDE by a hybrid film was carried out in several stages. In the first step, an amino group from a solution containing 0.1 M NaNO_2 , 20 mM 4-aminobenzylamine, and 0.5 M HCl was introduced on the surface using a CV from +0.6 V to -1.0 V. Then, the solution containing MWCNTs and tyrosinase was applied to the functionalized BDDE and allowed to dry [131]. Brycht et al. modified BDDE with MWCNTs and β -cyclodextrin. A suspension containing MWCNTs and Nafion was applied onto the prepared BDD surface and subsequently left to dry. In the second step, β -cyclodextrin was electrochemically precipitated from a solution containing this substance in BRB (pH 4.0); the optimal deposition potential being -0.2 V. This modification was used for voltammetric determination of fungicide *Carbendazim* [132].

In recent years, there have also been studies focused on the preparation of the so-called hybrid electrodes combining the properties of BDD and various sp^2 carbon materials, such as graphene or different carbon nanomaterials. In this case, it is not a modified BDDE, but both materials are synthesized simultaneously in the electrode manufacturing process. An example is the boron-doped diamond / graphene nanowall electrode (B:DGNW), which combines the excellent properties of BDD with graphene nanowalls upon one surface. B:DGNW was synthesized using a CVD method. Such an electrode was successfully used to determine 2,4,6-trinitrotoluene and 2,4,6-trinitroanisole in liquid effluents [133] or 4,4',5,5'-tetranitro-1H,1'H-2,2'-biimidazole [134]. Siuzdak et al. prepared novel materials called boron-doped diamond/carbon nanowalls (B:DCNW) applying microwave plasma-assisted CVD in a gas mixture containing of H_2 , CH_4 , B_2H_6 , and N_2 . The resultant form is CNWs rich in both sp^2 and sp^3 hybridized phases.

B:DCNW was applied for the electrochemical determination of guanine and adenine [135]. A different approach represents an electrochemical sensor, which contains patterned sp^2 -carbon regions in a BDD matrix. Lucio et al. prepared such electrode by laser micromachining. They demonstrated that this electrochemical sensor can be used for the quantitative detection of OCl^- at high concentrations in the challenging environment of industrial grade bleach solutions [136].

Table 4 Modification of BDDE by carbon materials and their application

Type carbon	Modification procedure	Application	Reference
Nano-carbon Black	The solution applied to the electrode surface and dried	chlorogenic acid	[123]
Graphene	Electrodeposition (AcBS (pH 5.6); graphene oxide; -1.2 V)	carbaryl, paraquat	[125]
Graphene	Magnetron sputtering followed by annealing and etching	lead ions	[126]
Ag-graphene	Electrodeposition (not specified; $AgNO_3$; -1.2 V)	carbaryl, paraquat	[127]
AuNP-CS	The solution applied to the electrode surface and dried	organophosphate pesticides	[128]
Chitosan-CNT-AuNP	The solution applied to the electrode surface and dried	catechol	[36]
NiNP-CNT	Ni film: DC magnetron sputtering. CTN: CVD	glucose	[129]
MWCNT-Nafion	The solution applied to the electrode surface and dried	ciprofloxacin	[130]
MWCNT-Tyrosinase	The solution applied to the electrode surface and dried	bisphenol A	[131]
β -cyclodextrin-MWCNT	The solution applied to the electrode surface and dried, electrodeposition of β -cyclodextrin (BRB (pH 4); -0.2 V)	carbendazim	[132]
GNW	CVD	2,4,6-trinitrotoluene, 2,4,6-trinitroanisole	[133]
GNW	CVD	4,4',5,5'-tetranitro H,1'H-2,2'-biimidazole	[134]
CNW	CVD	guanine, adenine	[135]
sp^2 -carbon	Laser micromachining	OCl^-	[136]

Abbreviations: GNW – graphene nanowall; CNT – carbon nanotube; CNW – carbon nanowall; CS – carbon spheres; MWCNT – multi-walled carbon nanotubes; NP – nanoparticle

Conclusions

It is well known that boron doped diamond electrode (BDDE) exhibits exceptional electrochemical properties that make BDDEs widely used in the field of applied electrochemistry. Moreover, it was documented in this review that it is also an excellent substrate for modifications, both with metallic or carbon nanomaterials and with organic molecules and biomolecules as well. Various modifications lead to improve electrochemical properties, in particular selectivity and sensitivity of the analysis. Electrocatalytic properties are usually a benefit of metal nanoparticles. In particular, carbon nanomaterials bring a significant increase of the electroactive surface area. Modifiers based on organic substances, polymers and biomolecules, most often lead to increase the selectivity. The modified BBDEs can be also successfully used in the preparation of biosensors.

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