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Boron-Doped Diamond Electrodes: Recent Developments and Advances in View of Electrochemical Drug Sensors

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ABSTRACT

Conductive boron-doped diamond (BDD), in addition to its superior material properties, offers many important advantages that make it an interesting material for electroanalytical studies. It has been considered as an excellent electrode material for electrooxidation of drug active compounds in their dosage forms or in biological materials due to its good physical and chemical properties. It contains not only the largest solvent working potential window compared to other electrode materials, but also it has low background and capacitive currents; lower problems with passivation and it has the ability to withstand extreme potentials, corrosive, and high temperature/pressure environments. The aim of this review is not only to provide a state-of-the-art of diamond electrochemistry but also to serve as a reference point for any researcher wishing to commence work with diamond electrodes and understand electrochemical data. Therefore, it is focused on the carbon-based materials, electrochemical properties of the BDD film electrode, its fundamental research, and its electrochemical pretreatment process are discussed in detail. In this case, there are important studies to show the effective BDD drug sensors for the detection and determination of drugs and the present review critically summarizes the available data in this field between 2015 and 2020.

KEYWORDS

Boron-doped diamond; pretreatment; carbon materials; drug analysis; voltammetry

Introduction

Carbon materials generally exhibit beneficial properties due to their characteristics, such as wide potential range, affordable cost, chemical stability, etc. Electrocatalytic activities of carbonaceous materials contribute to electrochemical analysis for detecting and/or identifying biological and environmental materials. Pyrolytic graphite, graphene, carbon dots, carbon nanotubes (CNT; SWCNT, MWCNT), diamond like carbon, fullerene, and carbon nano-onions (multi-layer fullerenes) are examples of novel carbon materials (Figure 1). Graphene, CNTs, and boron-doped diamond (BDD) have been widely used as electrode surface because of their polymorph properties such as large surface-to-volume ratio, high conductivity, and electron mobility for electrochemical sensing in recent years.[1] Electrochemical behavior of $-sp^3$ hybridized carbon as diamond and sp^2 hybridized carbon as graphene can change with doping by boron.

Exceptional electroconductive features of carbon have led it to its use both as modification agents and electrode materials in electroanalysis.[2] Although glassy carbon electrode (GCE) is the most popular and widely used carbon-based electrode; other carbon-based electrodes which take advantage of different carbon forms such as carbon paste electrodes, screen-printed carbon electrodes, and boron-doped diamond electrode (BDDE) that receive an increasing attention nowadays, have an incontrovertible place in electrochemical sensor applications.[3,4] BDDE have been investigated since 1980s, on the other hand it was in the 1990s that the interesting electrochemical properties of electrodes based on BDD, as a new form of carbon, began to gain wide coverage in research.[4,5]

BDDE whose semiconductor property was provided by boron doping has stability, biocompatibility, low capacitance, and wide electrochemical window and it is a frequently preferred electrode for the electrochemical analysis of numerous chemical compounds.[6,7]

Electroanalytical properties of BDDE are affected by various parameters such as boron/carbon ratio, $sp^3/sp2$ ratio and surface termination.[6] Potentiostatic/potentiodynamic, galvanostatic, and current pulse pretreatment procedures can be applied to BDDE.[4] All these important parameters and pretreatment strategies will be explained in the following sections. In addition to these; important points about major techniques such as high pressure high temperature (HPHT) and chemical vapor deposition (CVD) for BDD synthesis will be given.[8]

Bare BDDE as well as modified BDDE have been widely employed in electrochemical drug analysis due to unique electrochemical characteristics of BDD.[7] This review provides a comprehensive summary of the studies between the years 2015 and 2020 on the electrochemical applications of

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both bare and modified BDDE for the determination of drugs in biological and real samples.

A unique carbon material: diamond

Carbon and its different allotropes and forms have always been widely researched and used materials due to their versatility and advantageous chemical, physical, optical, and electrical features.[9] Before explaining the unique carbon material diamond, it is necessary to project a perspective on other carbon materials to be able to compare them with diamond.

Graphene

Graphene is described as a 2D and zero-gap semiconductor material. It exhibits many electrical, optical, mechanical, and metallic properties, such as high electron mobility and atomic sized thicknesses (<1 nm), etc. Modification of electrodes with 2D materials synergistically improve the electrocatalytic activity, conductivity, selectivity, and biocompatibility of the transducer. Graphene oxide, reduced graphene oxide, and functionalized graphene are other forms of graphene that can be synthesized in order to improve the electroconductive properties and achieve desired morphology.[10,11] Graphene, 2D material, can be used as flexible wearable sensor devices for clinical testing and biological monitoring.[12] Graphene and other graphene-based materials are also employed in gene therapy, drug delivery, imaging, and as antibacterial agents.[13] In the literature; there are several studies that aim to enhance reproducibility, response accuracy, and catalytic capability of the sensor by integrating unique features of graphene and BDD with graphene modification of BDDE.[14–16]

Carbon nanotubes

Carbon nanotubes were originally described in 1991 by Sumio Iijima. CNTs can be divided into two main types namely, single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). Rolling a graphene sheet into a cylinder results in SWCNT, on the other hand arrangement of concentric graphene cylinders with an interlayer space of 0.34 nm leads to the formation of MWCNT. CNTs show excellent chemical stability, good mechanical strength, and a wide range of electrical conductivity properties. These properties make them suitable for electrochemical applications.[17]

SWCNTs, MWCNTs, and their functionalized forms can be considered as the most frequently used modification agents for electrochemical drug sensors due to their unique electrochemical activity, conductivity, and stability.[18] They are also preferred for the modification of BDDE in sensor applications.[19]

Diamond

Diamond cannot be used as an electrode material because it is an insulator. However, diamond firstly introduced as an electrode material in different forms by Iwaki et al., in 1983[20] and then by Pleskov et al., in 1987.[21]. The sp3 carbons, including single crystal diamond and microcrystalline, nanocrystalline, and ultrananocrystalline diamond thin films can be devised with doping boron by applying the CVD technique. Therefore, diamond film can be semi-conductive (p-type), semi-metallic, or superconductive. Microcrystalline diamond exhibits grain size larger than 1 μm with large roughness, nanocrystalline diamond possesses between 10 nm and 1 μm sizes with moderate amount sp^2-bonded carbon boundaries. Ultrananocrystalline diamond has extremely low size (<10 nm) and roughness (<100 nm). Moreover, these properties give opportunity for the incorporation of graphitic carbon.

The use of diamonds in electrochemical devices: BDDEs

All of the allotropes of carbon, including diamond, have different chemical, electronic, and physical properties. Great thermal conductivity and mechanical strength are the distinguishing features of diamond. However, as a disadvantage diamond possesses very low conductivity. Nevertheless, at this point BDD is preferred as an option to enhance conductivity of diamond to the level that will be sufficient for electrochemical applications.[9]

From last five decades till now electrochemical devices are performed as cost-effective routine screening tools, serving as alternative methods to the traditional ones. Diamond electrochemistry using planar macroscopic diamond films has been widely investigated. Due to the non-uniform doping in diamond, boundary effects, and the varied ratios of graphite to diamond, such systems only provide average electrochemical signals over the full electrode. To clarify electrical and electrochemical properties of diamond at the nanoscale, the use of diamond nanostructures (e.g. nanotextures, nanowires, networks, porous film, nanoelectrodes, etc.) and particles (e.g. undoped nanoparticles, boron-doped particles), is highly important.[21] BDD, which has fast charge-transfer kinetic, low background currents, weak molecular adsorption, and extensive potential window, is a highly attractive electrode material depending on the boron-doping level and content of non-diamond carbon phase.[4,22,23]

In comparison with carbon-based and metallic electrodes, BDD electrodes has some unique advantages. The main distinguishing features of BDD electrode are very low and stable background current, largest potential window in aqueous and non-aqueous media and high sensitivity. The potential window of a phosphate buffer solution (pH 7.4) with BDD electrodes is extremely wide, and the background current is low (Figure 2). These differences make BDD electrode suitable in several applications with enhanced signal to noise ratio (*S*/*N*). General problem of GCE is easy fouling which restricts their electrochemical stability. However, BDD electrode has low fouling resulting in the possibility of the long-term use and extreme electrochemical response stability. Other important advantages of the BDD electrode are tunable electrochemical properties by the boron concentration,

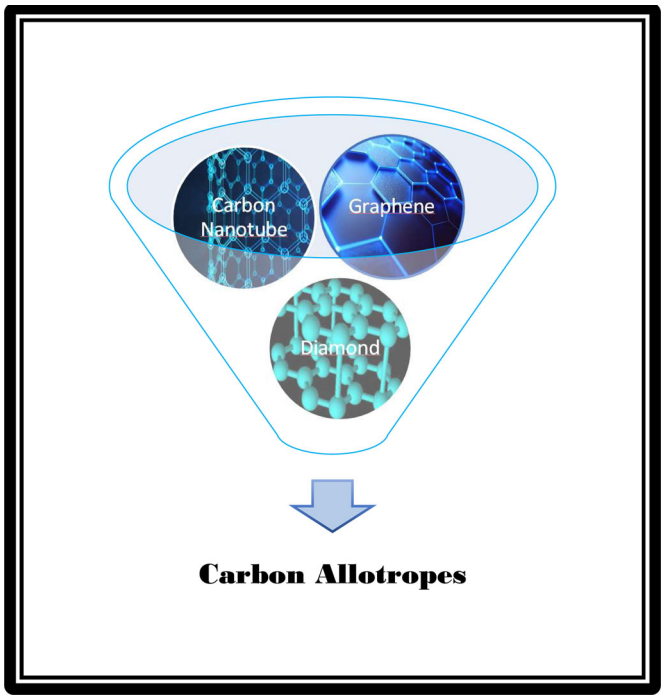


Figure 1. Different types of electrode surface materials.

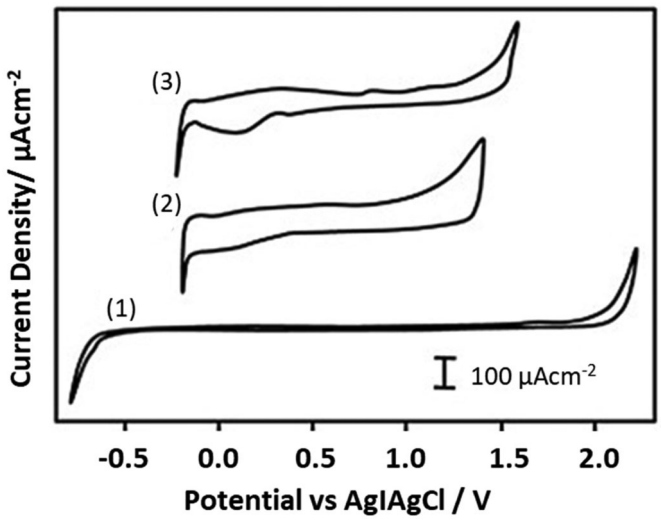


Figure 2. Potential windows of various electrodes in 0.5 M H_2SO_4 (BDDE with (1) low sp2 content, (2) high sp2 content and GCE (3)). Reprinted from Ref. [25] after permission from Elsevier.

low magnetic susceptibility, good biocompatibility, high thermal conductivity, extreme hardness, and chemical inertness.[6,22,24]

Synthesis and preparation of BDDE

Due to complete C-sp^3 hybridization, strong and covalent tetrahedral bonding of diamond, it provides some desirable properties such as high melting point, extreme hardness, and low friction coefficients.[6,26] Also, diamond has been known as an electrical insulator, as it has completely filled valence band and empty conduction band, very wide band gap (5.47 eV at $T = 300$ K), and high electrical resistivity

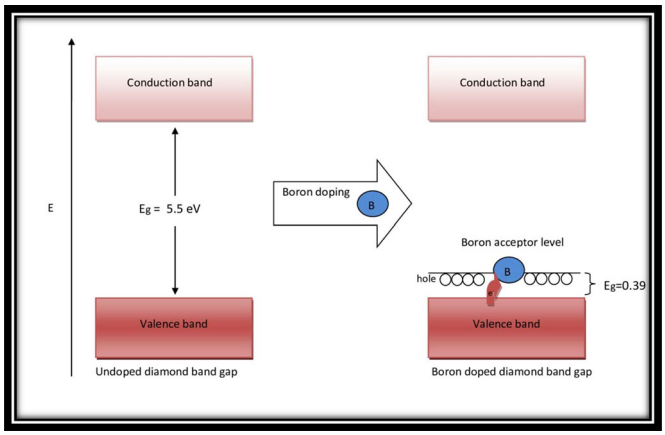


Figure 3. Band gap diagram of undoped and boron-doped diamond.

($10^{16}\,\Omega$ cm) as shown in Figure 2.[6,27] However, it is easily converted to its electrically conductive form with introduction of dopant atoms. Substitutional doping atom forms new energy levels in the band structure giving a p- or n-type-conducting characteristic into diamond lattice. This characteristic aspect depends on the type of dopant atoms (charge carriers). By introducing p-type dopants like B and Al with impurity atoms, free electrons result in acceptor energy level (0.37 eV) above the valence band of diamond that is shown in Figure 3. Introduction of n-type dopants like N and P results in donor energy level whose additional free electrons can be easily transferred into conduction band of the diamond. These holes can be filled with electrons, which are promoted from valence band of diamond to acceptor level of boron; therefore, this electron movement in the valence band enhances conductivity of diamond lattice. The most applicable and successful dopant atom is boron, because it has one less electron than carbon and has small atomic radius so it can be easily doped into diamond.[22]

HPHT and CVD methods are the main growth techniques that are used for the synthesis of doped diamond materials. HPHT has been used for the synthesis of diamond for many years. With HPHT, diamond is synthesized under high temperature (1800 K) and high pressure (3–5 GPa).[8] CVD is vacuum deposition method on the surface of support materials seeded with diamond nanoparticles under plasma conditions from carbon-containing gas mixture (methane) and boron gas (diborane) in the presence of hydrogen.[28] There are many surface support materials such as Silicon (Si), Titanium (Ti), Niobium (Nb), Tungsten (W) used for enabling electrons to move into electrode array and provide mechanical strength and stability for the BDD thin films. Generally, many substances are grown on a flat surface material. Nevertheless, this technique enables flexible electrode production *via* the transfer of BDD to flexible substrates.

The microwave plasma-assisted CVD (MWCVD) and the hot filament CVD (HFCVD) are common CVD techniques for the synthesis of BDD thin films.[29–31] HFCVD uses hot filament to activate the boron containing gas compounds that chemically decompose on the surface of support material. Phosphorus and nitrogen (charge carrier activation energy 1.6–1.7 eV) are also known as diamond dopants,

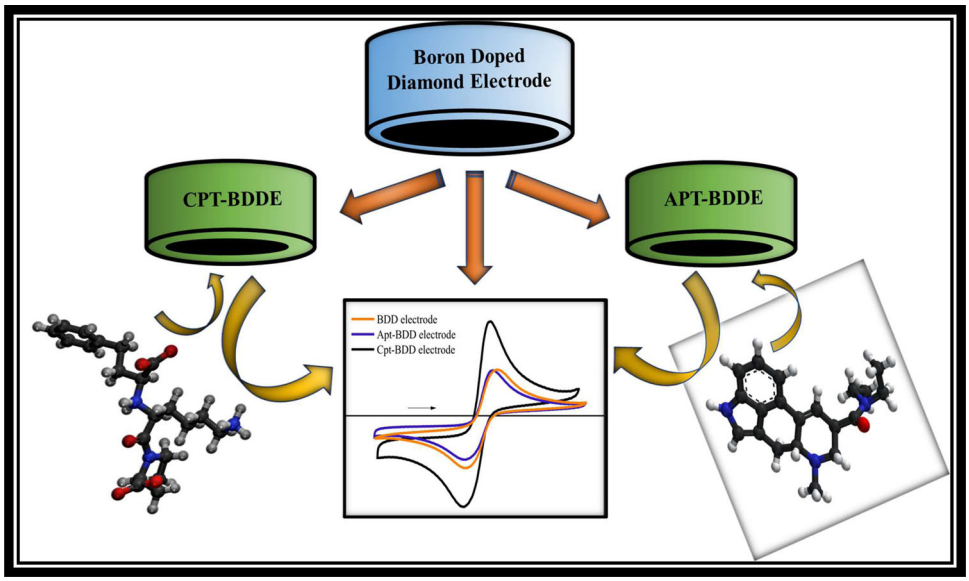


Figure 4. Voltammograms of basically electrochemical pretreatments applied BDDE. Partly used from Ref. [37] with permission from Elsevier.

expanding material applications. Introduction of sulfur into diamond is only possible in the presence of boron. MWCVD uses microwave radiation that forms microwave generated plasma enhances the chemical reaction rate.

BDDE can be prepared using p-type semiconducting BDD thin films. BDD thin films are obtained by substituting some of the sp^3 hybridized carbon atoms in the diamond lattice with boron atoms.[24] Generally, BDD thin films are obtained by two doping ways, which are *in situ*, and *ex situ* doping. For *in situ* doping, boron containing gas precursors like diborane (B_2H_6) and trimethylborate $B(OCH_3)_3$ have been introduced while synthesizing diamond films *via* CVD. *Ex situ* doping use, ion implantation boron doped into already synthesized diamond thin films.[28]

Growth of diamond by CVD enables BDD thin films to obtain different crystalline sizes like polycrystalline and nanocrystalline films and change boron-doping level in the gas phase. Therefore, surface structure and electrical property of BDD electrode can be controlled. The most used BDD electrodes are the polycrystalline form because of the relative ease at which they can be produced over different length scales.[28]

In addition, there are two methods, which are ion implantation and thermal diffusion for doping diamond. Ion implantation needs high annealing temperature so it is a problematic process. Thermal diffusion is not a cost-effective method because it requires long diffusion process that results in less boron-doped layers.

Important parameters influencing the performance of BDDE

BDDE are made up of solid materials. They possess remarkable electrical conductivity, electrochemical stability, fast electron transfers, and reproducible electrical and chemical features, when compared with other carbon electrodes such as GCE and highly-oriented pyrolytic carbon (HOPG).

BDDE are utilized in microlithographic fabrication of microelectrodes. Unlike macroelectrodes, microelectrodes exhibit sigmoidal voltammogram. Different parameters such as boron concentration, chemical and physical structure, and applied operational conditions during pretreatment affects the electrochemical performance of BDDE.

Boron-doping concentration

As mentioned before, when diamond lattice is doped with boron atoms, p-type semiconductor BDDE forms. Boron-doping concentration affects the conductivity of the electrode like insulator to metal. Diamond possesses numerous attractive features of an excellent working electrode material in electrochemistry. When the doping concentration of the electrode increases, electrical resistivity decreases. Boron-doping concentration can be changed from 10^{18} to $10^{21}\,cm^{-3}$ in diamond lattice and this boron doping decreases the resistivity of diamond from 10^{16} to $10^{-2}\,\Omega\,cm$.[7,27] In addition, boron-doping concentration varies from low temperature to higher temperature condition. When boron-doping concentration is $3.92 \times 10^{21}\,cm^{-3}$, metal to insulator transition takes place at low temperature.[32] However, if doping concentration is lower, BDD shows room temperature conductor or semiconductor properties.[33] Thus, due to the doped atom concentration changes, BDD can be known as semi-metalic (10^{17} atom cm^{-3}) or metal-like (10^{20} atom cm^{-3}).[12] $10^{20}\,cm^{-3}$ boron-doping concentration is generally enough for BDD to get good conductivity and to be used in electrode applications. This doping concentration level equals to roughly 1:100 boron to carbon ratio.[33] Therefore, by introducing boron doping, holes form as mobile charge carriers in diamond to allow current flowing. In addition, boron-doping concentration has an effect on the color of BDD. Doping boron into diamond results in visible color change because of new dopant energy level absorbing visible light. Semiconducting BDD shows a blue color and conducting BDD seems to be black.[28] Depending on how the BDD electrode surface is

magnified and then processed prior to electrochemical measurement, the resulting material properties and electrochemical response can vary considerably. Hence, this point has explained the variability seen by different researchers working on the same experimental systems.

Pretreatment process

Electrochemical responses of many redox species depend on the fact that the surface is predominantly hydrogen- (HT) or oxygen-terminated (OT). The surface of *in situ* BDDE is enriched in the means of pretreatment. Moreover, a simple electrochemical pretreatment is considered environment-friendly because of the reduced use of hazardous chemicals and a simple procedure that takes less than 5 min compared with other different modification materials.[34] Anodic (APT) or cathodic (CPT) pretreatments, which are usually used for electrochemical pretreatment of BDDEs, are depicted in Figure 4. The surface of a cathodically pretreated BBDE (CPT-BDDE) becomes enriched in HTs, whereas that of an anodically pretreated BDDE (APT-BDDE) becomes enriched in OTs for yielding enhanced sensing properties.[4]

Electroactive area and electron transfer rate increased with electrochemical activation of BDDE. BDDEs are reported to exhibit low background current as well as stable and reproducible response over long time periods. Cobb et al. referred about a recent study of designing BDDE in their article.[35]

sp^3/sp^2 ratio

BDD synthesis generally results with the formation of a material which can be described as the combined forms of sp^3 and sp2 carbons. sp3 carbon phase is the catalytically inert carbon while sp^2 phase is the non-diamond and amorphous one. Despite the fact that sp^2 carbons are considered as impurities it is possible to use them for adjustment of some performance parameters of BDDE. The presence and ratio of sp^2 impurities are adjusted in the fabrication and it should be done carefully. sp^2 carbons can provide catalyzed redox reactions with increased electron transfer rate. Nevertheless, they can also cause reduced resistance against corrosion and narrow electrochemical window with increased background currents.[6]

Electrochemical sensor applications of BDDE

BDDE can help solving some of our environmental problems and also improve our quality of life through their use in biomedical devices.[37] Moreover, BDDE are widely used in electrochemical sensing, electroanalysis, and electrochemical synthesis.

In this section, most recent and selected electrochemical applications of BDDE are emphasized. In Tables 1 and 2, the published papers are brought together and categorized based on the applied electrochemical methods and sample applications; obtained potential, recovery, linearity range, and LOD/LOQ results. In addition to this, Table 1 only focuses on the applications of only bare BDDE while Table 2 summarizes the studies on electrochemically pretreated BDDE.

Morawska and coworkers studied electrochemical behavior of the antiviral drug tenofovir disoproxil (TNF) on a BDDE. In addition, a quantitative analysis of the pharmaceutical formulations and TNF showed the biological importance of the developed method. Interactions between DNA and TNF were studied using voltammetric and spectrometric methods. The appropriate SWV response of TNF was obtained with a BRB at pH 4.0 on BDDE. The use of SWV with the optimized parameters ($f = 10$ Hz, $a = 40$ mV, and $\Delta Es = 5$ mV) revealed that the oxidation of TNF occurring on the BDD electrode surface was diffusion-controlled. A reduction peak was obtained at -1.5 V. This study showed the determination of TNF in two pharmaceutical formulations, that is, TNF, with satisfactory recoveries in the range of 101.9% and 95.8%, respectively. The correlation coefficient in the linear range of 5–100 µM was found as 0.9999. Limit of detection (LOD) and limit of quantification (LOQ) values were estimated as 0.56 and 1.9 μM, respectively. The results reported here showed the efficiency and the applicability of the use of BDDE connected to electrochemical techniques for determination of TNF.[94]

In another study, a simple, sensitive, and low-cost voltammetric method using BDDE was developed for the determination of desloratadine (DES) in human urine and tap water samples by Nagao et al. DES provided an irreversible oxidation peak at a potential of 1.55 V versus Ag/AgCl/KCl (3 mol L^{-1}) electrode in phosphate buffer solution (PBS, pH 4.0). Under optimal experimental conditions, DPV was used for the determination of DES. DPV was proposed for the sensitive determination of DES in a linear concentration range from 0.099 to 6.3 µM, with a detection limit of 41.0 nM and a good repeatability (RSD of 1.85%). The developed methods were applied to analysis of the human urine and tap water samples with the recoveries from 92.7% to 103.0% and from 98.4% to 107.0%, respectively. Unmodified BDDE showed great sensitivity with good reproducibility and stability, good selectivity, and low detection limit for DES determination.[104]

Pereira et al.[139] described the development of a method for voltammetric determination of pindolol in pharmaceuticals and biological fluid samples using a CPT-BDDE. Comparatively, the use of CPT-BDDE provided a limit of detection value ~3.7 times lower than the attained by Cumba et al.[142] by SWV using a screen-printed graphite electrode; ~2.0 times lower than the attained by Tadi and Motghare[143] by adsorptive stripping differential pulse voltammetry using a molecularly imprinted polymer carbon paste electrode; and similar to the one attained by Smarzewska and Ciesielski[144] by square-wave striping voltammetry using a GCE modified with RGO.

Immobilization of biomolecules on solid platforms is important for the improvement of stability of biosensors and biochips. Protein and DNA linked to glass, silicon, and gold surfaces may decrease in stability over time. Therefore, Hamers and coworkers gave the suggestion that diamond is an ideal material for future biochips because of its superior properties.[145] Due to the inert nature of diamond surfaces, the immobilization of biomolecules on diamond for the

Table 1. Selected electroanalytic studies of drug components on bare BDDE.

Active compound	Method	Potential of peak (V)	Linearity range	LOD or LOQ	Buffer or media	Application	Recovery (%)	References
Paracetamol Caffeine	CV-DPV-SWV	0.550	0.5–8.3 μM	0.49 μM (LOD) 0.035 μM (LOD)	pH 4.5 Acetate buffer	Pharmaceutical formulations	97.7–99.0	[38]
Sertindole	SWV DPV	1.04 1.08	4 μM–0.2 mM 4 μM–0.1 mM	0.217 μM (LOD) 0.240 μM (LOD)	pH 3.5 Acetate buffer	Serum samples	100.64–100.9	[39]
Sulfamethoxazole trimethoprim	DPV	0.92 1.1	1–10 mg L^{-1} 2–10 mg L^{-1}	3.65 μg L^{-1} (LOD) 3.92 μg L^{-1} (LOD)	0.2 M pH 7 BRB	Pharmaceutical formulations	92.4–105.0 88.8–107.0	[40]
Ascorbic acid Acetaminophen	CV-DPV	0.4 0.6	0.01–0.1 mM	1.31 μM (LOD) 1.50 μM (LOD)	0.1 M pH 7 Na_2SO_4	Pharmaceutical formulations	–	[41]
Acetylsalicylic acid	SWV	1.97	2.5 μM–0.105 mM	2.0 μM (LOD)	0.01 M H_2SO_4	Pharmaceutical formulations	93.3–107.0	[42]
Lercanidipine	SWV	0.944	4.0–200.0 μM	0.690 μM (LOD) 2.06 μM (LOQ)	0.5 M H_2SO_4	Pharmaceutical formulations Serum samples	100.06 99.64–100.01	[43]
Ascorbic acid Caffeine	DPV	0.81 1.36	19 μM–0.21 mM 9.7 μM–0.11 mM	19 μM (LOD) 7 μM (LOD)	0.1 M H_2SO_4	Pharmaceutical formulations	96.4–97.3	[44]
Sildenafil citrate	CV-DPV	1.40	0.73–7.3 μM	0.64 μM (LOD)	0.1 M H_2SO_4	Pharmaceutical formulations	91.5–101.0	[45]
Propranolol Atenolol	CV-SWV-DPV	1.2–1.15 1.67–1.60	0.20–9.0 μM 2.0–41 μM	0.18 μM (LOD) 0.93 μM (LOD)	0.1 M H_2SO_4 0.5 M $NaNO_3$	Pharmaceutical formulations	93.9–105.0 92.5–106.0	[46]
Estriol	SWV	0.38	0.20–20.0 μM	0.17 μM (LOD) 0.85 μM (LOQ)	pH 12 NaOH	Pharmaceutical formulations; Urine samples	98.6–101.0 100.2–103.4	[47]
Fulvestrant	CV-DPAdV	1.10	1.0–80.0 μM	0.236 μM (LOD) 0.788 μM (LOQ)	1 M H_2SO_4	Pharmaceutical formulations; Serum samples	100.88 100.25	[48]
Ezetimibe	DPV SWV	1.12–1.16	2.0–100.0 μM	0.227–0.245 μM (LOD) 0.688–0.741 μM (LOQ)	0.1 M H_2SO_4	Pharmaceutical formulations; Serum samples	100.39–100.56 99.80–100.04	[49]
Sildenafil Vardenafil	Amperometry	1.520	10–400 ng mL^{-1}	2–4 ng mL^{-1} (LOD) 7.0–13.4 ng mL^{-1} (LOQ)	40 mM pH 3.5 $NaClO_4$–CH_3CN	Human plasma	–	[50]
Varenicline	SWASV	−0.53	0.5–5 μM	0.71 μM (LOD) 2.4 μM (LOQ)	pH 3.5 BRB	Plasma samples; Pharmaceutical formulations	100.2–102.0 99.8–101.7	[51]
Metoclopramide	DPV FIA-Amperometry	0.90	0.1–10 μM	0.13 μM (LOD) 0.015 μM (LOD)	pH 6 BRB	Pharmaceutical formulations	–	[52]
Caffeine Acetylsalicylic acid	DPV	1.35 1.46	1.0 μM–1 mM 0.1 μM–1 mM	0.16 μM (LOD) 0.23 μM (LOD)	0.1 M H_2SO_4	Pharmaceutical formulation	100.0	[53]
Penicillin V	DPV	1.60	0.5–40 μM	0.25 μM (LOD)	pH 4 Acetate buffer	Pharmaceutical formulations; Urine samples	98.0–101.0 97.0–103.0	[54]
Paracetamol Penicillin V	SWV	0.35	0.4–100 μM	0.21 μM (LOD) 0.32 μM (LOD)	pH 5 Acetate buffer	Urine samples	95.0–101.0	[55]
Melatonin hormone	SWV	0.88	5.0×10^7 M–4.0×10^6 M	1.1×10^7 M (LOD)	pH 3 BRB	Pharmaceutical formulations; Urine samples	97.67–105	[56]
Brimonidine	DPV SWV	−0.375	2.0–30 μM 0.5–15 μM	0.631 μM (LOD)–2.1 μM (LOQ) 0.128 μM (LOD)–0.428 μM (LOQ)	0.1 M H_2SO_4	Pharmaceutical formulations	98.0–102.0	[57]
Codeine	DPV	0.97	0.1–60 μM	0.08 μM (LOD)	pH 7 BRB	Pharmaceutical formulations	96.2–102.6	[58]

α-Tocopherol	CV	0.60	0.5–100 μM	41 nM (LOD)–138 nM (LOQ)	50 mM $NaClO_4$–Methanol	Human plasma	–	[59]
Ubiquinone		0.50	0.5–100 μM	17 nM (LOD)–54 nM (LOQ)				
Nimesulide	CV-MPA	−0.70	10–50 mg L^{-1}	0.297 mg L^{-1} (LOD)	0.1 M H_2SO_4	–	–	[60]
Paracetamol		0.90	50–250 mg L^{-1}	0.293 mg L^{-1} (LOD)				
Hydrochlorothiazide	DPV	0.23	4–83 μM 3–74 μM	1.2 μM (LOD)	pH 9.5 BRB	Pharmaceutical formulations	98.0–102.0	[61]
Losartan				0.95 μM (LOD)				
Tryptophan	CV-DPV	0.98	50–500 μM	0.5 μM (LOD)	0.1 M KCl-pH 7.4 aqueous solutions	Human serum samples	–	[62]
Tyrosine		1.11		0.2 μM (LOD)				
Terbinafine	SWV	0.92–0.96	0.544–5.18 μM	0.164 μM (LOD)–0.495 μM (LOQ)	pH 6.09 BRB	Pharmaceutical formulations	100.29–101.41	[63]
	DPV		0.775–8.55 μM	0.236 μM (LOD)–0.718 μM (LOQ)				
Captopril	SWV	1.00	20–100 mg L^{-1}	36.0 μg L^{-1} (LOD) 121.95 μg L^{-1} (LOQ)	pH 9 BRB	Pharmaceutical formulations	96.6–98.5	[64]
Paracetamol	DPV	0.85	20–400 μM	7.1 μM (LOD)	0.1 M H_2SO_4	Pharmaceutical formulation	100.0	[65]
Ibuprofen		1.72		3.8 μM (LOD)				
Amlodipine	CV-DPV	0.75	0.2–6 μM	0.07 μM (LOD)	pH 5 BRB	Pharmaceutical formulations; Urine samples	101.3–104.1 94.1–105.7	[66]
			6–38 μM					
Hydroxychloroquine	CV-SWV-CA	1.52	0.1–1.9 μM	0.06 μM (LOD)	0.1 M H_2SO_4	Synthetic urine samples	95.0–100.0	[67]
Hydrochlorothiazide	CV-SWV-CA	1.14	1.97–88.1 μM	0.639 μM (LOD)	pH 5 BRB	Pharmaceutical formulations	101.0	[68]
Valsartan		1.42	9.88–220 μM	2.13 μM (LOQ) 0.935 μM (LOD) 3.13 μM (LOQ)			98.3	
Ambroxol	SW-AdSV	1.03	0.05–0.7 μM	0.010 μM (LOD)	pH 2.5 PB	Urine samples	106.0	[69]
Adrenaline	CV-SWV	0.75	0.7–60 μM	0.21 μM (LOD)	0.5 M $HClO_4$	Urine samples	98.0–102.0	[70]
Theophyllin	DPV	1.63	2–380 μM	0.91 μM (LOD)	1.0 M H_2SO_4	Pharmaceutical formulations; Urine samples	98.0–103.3 93.2–102.2	[71]
	SWV			1.45 μM (LOD)				
Trifluoperazine	CV-DPV	0.65–0.83–1.06–1.35	1.0–37.0 μM	0.6–0.7 μM (LOD)	pH 6 BRB	Urine samples	97.0–104.0	[72]
Levomepromazine	SWV-DPV	0.516–0.488	0.4 μM–0.602 mM	0.128–0.292 (LOD)	0.1 M $HClO_4$	Pharmaceutical formulations	98.52–99.57	[73]
Promazine		0.545–0.493	0.4 μM–0.196 mM	0.389–0.885 (LOQ)				
Prothipendyl		0.604–0.560	0.495–95.4 μM	0.129–0.294 (LOD) 0.391–0.892 (LOQ) 0.160–0.386 (LOD) 0.485–1.17 (LOQ)				
Aliskiren	CV-SWV	1.10	18.1 μM–0.163 mM	25 nM (LOD) 84 nM (LOQ)	0.04 M pH 8 BRB	Pharmaceutical formulations; Serum samples	98.2–100.2 95.5–97.8	[74]
Rapamycin	CV-DPV	1.10	0.5–19.5 μM	0.22 μM (LOD)	pH 3 BRB	Urine samples; Blood serum samples	96.35–107.2 101.3–106.3	[75]
Pyridoxine (Vitamin B_6)	DPV	1.05	7–47 μM	3.76 μM (LOD)	pH 6 BRB	Pharmaceuticals formulations; Urine samples	102.0–105.0 100.0–101.0	[76]
7-Methylguanine	CV-SWV	0.803–10.5	1.65–33 μg mL^{-1}	2 μg mL^{-1} (LOD)	0.1 M pH 5 Acetate buffer	Urine samples	–	[77]
Omeprazole	CV-LSV	0.968–1.068	1.2–6.9 μM	0.091 μM (LOD)	pH 3–9 PBS	Urine samples	98.6–102.9	[78]
Metronidazole	CV-SWV	−0.90–(−0.95) –(−1.02)	0.2–4.2 μM	0.065 μM (LOD) 0.2166 μM (LOQ)	0.29 M Na_2SO_4	Urine samples	98.5–102.5	[79]
Ramipril	CV-SWV	1.23	1.96–36.7 μM	0.027 μM (LOD)	pH 2 BRB	Pharmaceutical formulations	102.0	[80]
Hydrochlorothiazide		1.67	2.46–36.7 μM	0.0182 μM (LOD)			98.0	
Ciprofloxacin	SWV	1.15	0.15–2.11 μM	0.05 μM (LOD)	pH 5 Ammonium acetate buffer	Urine samples	97.0–102.0	[81]

(*continued*)

Table 1. Continued.

Active compound	Method	Potential of peak (V)	Linearity range	LOD or LOQ	Buffer or media	Application	Recovery (%)	References
Flutamide	DPV SWV	0.9–1.2–1.8 0.9–1.3–1.9	0.99–42.9 μM 4.8–35.5 μM	0.42 μM (LOD) 0.18 μM (LOD)	0.1 M H_2SO_4	Pharmaceutical formulations; Urine samples	95.6–106.4 39.9–106.3	[82]
Cephalosporins	CV-DPV	1.2–1.4	0.5–700 μM	34.74 ng mL^{-1} (LOD)	0.5 M H_2SO_4 0.2 M pH 4.5 Acetate buffer	Urine samples; Pharmaceutical formulation	93.41 92.40	[83]
Imipramine	SWV	0.04–0.82	0.173–2.53 μM	43.5 nM (LOD) 0.145 μM (LOQ)	0.04 M pH 7.4 BRB	Pharmaceutical formulation	95.5	[84]
Levofloxacin	CV-SWV	1.17–1.25–1.71	48–100 μM 10–80.9 μM	2.88 μM (LOD) 9.60 μM (LOQ)	1.4 mM Na_2SO_4	Serum samples	95.34–107.95	[85]
Bromazepam Alprazolam	DPV	−1.1 −0.84	1.0 μM–10 mM 0.8 μM–10 mM	0.31 μM (LOD) 0.64 μM (LOD)	pH 11 BRB pH 5 BRB	Pharmaceutical formulations	97.33–100.85 94.14–101.32	[86]
Carisoprodol Acetaminophen Caffeine	SWV	2.03 1.50 0.980	19.9–207 μM 2.99–283 μM 2.99–84.8 μM	3.11 μM (LOD) 0.768 μM (LOD) 0.771 μM (LOD)	pH 6 BRB	Pharmaceutical formulations	91.7–104.0 93.4–101.0 95.2–104.0	[87]
Cetirizine	DPV	1.20	67–540 nM	16 nM (LOD)	pH 8 PBS	Urine samples	95.0–101.7	[88]
Benzocaine	DPV SWV	0.74–0.87 0.73–0.89	0.1–400 μM 0.4–200 μM	80 nM (LOD) 100 nM (LOD)	pH 4 BRB	Pharmaceutical formulations; Urine samples	97.4–104.5 97.0–102.7	[89]
Leucovorin	DPV	NA	1000–20000 ppm	6.7 nM (LOD)	pH 3 BRB	Pharmaceutical formulations	97.7–103.3	[90]
Nifedipine Atenolol	DPV	0.97 1.36	3.98–107 μM 1.99–47.2 μM	0.612 μM (LOD) 0.999 μM (LOD)	pH 8 TRIS buffer solution	Pharmaceutical formulations	99.0–103.0	[91]
Ibuprofen	DPV SWV	1.75	0.949–66.9 μM	0.41 μM (LOD) 0.93 μM (LOD)	1 M $HClO_4$	Pharmaceutical formulations; Spiked urine samples	99.8–107.5 95.0–107.0	[92]
Leucovorin	DPV	0.9	0.15–25 μM	0.015 μM (LOD) 0.050 μM (LOQ)	pH 5 BRB	Pharmaceutical formulations	98.7–102.8	[93]
Tenofovir	SWV	1.5	5 μM–0.4 mM	0.56 μM (LOD) 1.9 μM (LOQ)	pH 4 BRB	Pharmaceutical formulations	95.8–101.9	[94]
Lamotrigine	CA	1.4	0.2–5 μM	29 nM (LOD)	0.1 M pH 7 PBS	–	–	[95]
Ascorbic acid	SWV	0.703	20–200 μM	1.87 μM (LOD)	BRB	Pharmaceutical formulations	–	[96]
Bisacodyl	DPV SWV	1.55–1.59	1–44 μM 1.99–21.9 μM	0.343 μM (LOD) 0.707 μM (LOD)	pH 5 BRB	Pharmaceutical formulations	99.1–102.3	[97]
Dipyridamole	DPV SWV	0.45	0.1–5.0 μM 0.1–6.0 μM	40 nM (LOD) 60 nM (LOD)	pH 3 BRB	Pharmaceutical formulations	95.8–96.6	[98]
Dipyrone	SWV	0.49	1.0–65 μM	0.26 μM (LOD) 0.880 μM (LOQ)	0.04 M pH 7 BRB	Urine samples	104.0	[99]
Mefenamic acid Indomethacin	DPV	0.6 1.1	0.5–100 μM 0.5–100 μM	0.078 μM (LOD) 0.054–0.074 μM (LOD)	pH 5 BRB	Pharmaceutical formulations	94.0–107.0 95.0–103.2	[100]
Cefixime	SWV	1.25	2.2–130 μM	0.59 μM (LOD)	0.1 M H_2SO_4	Pharmaceutical formulations	92.32–98.61	[101]
Acetaminophen Tramadol HCl	SWSV	1.04 1.61	6.6–460 μM 3.3–230 μM	0.73 μM (LOD) 0.43 μM (LOD)	0.1 M pH 3 BRB	Pharmaceutical formulations	96.4–98.8 91.6–95.7	[102]
Nefopam	DPV-SWV	1.7	2.00–59.7 μM 0.99–77.1 μM	0.5 μM (LOD)	1.0 M $HClO_4$	Pharmaceutical formulations Human Urine	98.0–95.6	[103]
Desloratadine	DPV	1.55	0.099–6.3 μM	41.0 nM (LOD)	pH 4 PBS	Urine samples	92.7–102.0	[104]
Meloxicam	DPV	0.9–1.4	0.25–85.0 μM	0.059 μM (LOD) 0.19 μM (LOQ)	pH 3 BRB	Pharmaceutical formulations	97.2–103.6	[105]

ASV, anodic stripping voltammetry; LSV, linear sweep voltammetry; CV, cyclic voltammetry; SWV, square-wave voltammetry; DPV, differential pulse voltammetry; CA, chronoamperometry; SW-AdSV, square-wave adsorptive stripping voltammetry; SWASV, square-wave anodic stripping voltammetry; ASV, adsorptive stripping voltammetry; DPAdV, differential pulse adsorptive stripping voltammetry; MPA, multiple pulse amperometry; BRB, Britton–Robinson buffer; PBS, phosphate buffer solution.

Table 2. Electroanalytical applications of electrochemically pretreated BDDEs for analysis of drug components.

Active compound	Method	Electrode	Potential of Peak (V)	Linear range	LOD/LOQ	Buffer or media	Application	Recovery (%)	References
Glucose	CV-LSV	BDNDE	0.63	0.25–12 mM	0.25 μM (LOD)	0.2 M NaOH	Blood samples	95.33–105.3	[106]
Glucose	Amperometry	Ni-BDDE	0.46	10 μM–0.01 M	2.7 μM (LOD)	1 mM pH 5 $Ni(NO_3)_2$	Blood samples	–	[107]
Tryptophan	DPV	BDD NWsE	0.6	0.5–50 μM	0.5 μM (LOD)	pH 11 Na_2PO_4–NaOH	–	–	[108]
Nitrofurantoin	SWV	BDDFE	−0.44	0.50–4.76 μM 0.50–5.66 μM	6.40–1.94 μg L^{-1} (LOD) 21.33–6.47 μg L^{-1} (LOQ)	pH 4 BRB	Pharmaceutical formulations	99.87–101.49	[109]
Sulfamethoxazole Trimethoprim	DPV	CPT/HT-BDDE	0.90 1.070	1.0–8.0 mg L^{-1} 0.2–1.6 mg L^{-1}	16.5 μg L^{-1} (LOD) 55.1 μg L^{-1} (LOQ) 18.3 μg L^{-1} (LOD) 61.1 μg L^{-1} (LOQ)	0.2 M pH 7 BRB	Pharmaceutical formulations	94.9–102.0	[110]
Ganciclovir	DPV	BDNDE	1.2	0.5–350 μM	0.2 μM (LOD)	pH 2.5 BRB	Serum samples	101.34	[111]
Bezafibrate	SWV	CPT-BDDE	1.20	0.10–9.1 μM	0.098 μM (LOD)	pH 2 BRB	Pharmaceutical formulations	93.4–108.0	[112]
Albendazole	DPV	CPT-BDDE	0.95–1.30	0.0797–8.36 μM	0.0625 μM (LOD)	0.05 M H_2SO_4	Pharmaceutical formulations	–	[113]
Paracetamol Caffeine Orphenadrine	SWV	CPT-BDDE	0.795 1.46 1.67	0.54–61 μM 0.78–35 μM 0.78–35 μM	0.23 μM (LOD) 0.77 μM (LOQ) 0.096 μM (LOD) 0.32 μM (LOQ) 0.084 μM (LOD) 0.28 μM (LOQ)	0.5 M H_2SO_4	Pharmaceutical formulations	92.6–104.0 95.0–107.0 95.3–103.0	[114]
Propylthiouracil	SWV-DPV	CPT-BDDE	1.37–1.30	1.0–29.1 μM	0.90 μM (LOD)	pH 2 BRB	Pharmaceutical formulations	97.1–104.6	[115]
Paracetamol Ascorbic acid	DPV	Nafion®-BDDE	0.47	0.5–200 μM 1–500 μM	0.17 μM (LOD) 0.52 μM (LOD)	0.1 M pH 6 Acetate buffer	Pharmaceutical formulations	100.04 97.73	[116]
Dopamine	CV-DPV	BDD-NEAs	0.4	0.1–20 μM	100 nM (LOD)	0.1 M PBS	–	–	[117]
Hydrochlorothiazide Enalapril	FIA-Amperometry	CPT-BDDE	1.70 1.90	0.40–8.00 μM 0.03–1.00 μM	0.20 μM (LOD) 0.01 μM (LOD)	0.05 M H_2SO_4	Pharmaceutical formulations	–	[118]
Amlodipine Valsartan	SWV	CPT-BDDE	0.791 1.37	0.497–28.0 μM 19.8–280 μM	0.0764 μM (LOD) 0.193 μM (LOD)	pH 5 BRB	Synthetic urine samples	93.9–105	[119]
Cholesterol	CV-CA	AgNP-BDDE	−0.71	0.39–270.69 mg dL^{-1}	0.25 mg dL^{-1} (LOD)	pH 7.4 0.05 M PBS	Bovine serum samples	99.6–100.8	[120]
Acetaminophen Tramadol	CV-Amperometry	CPT-BDDE	0.85 1.60	1.0–100 μM 0.08–10 μM	0.03 μM (LOD) 0.04 μM (LOD)	pH 2 BRB	Pharmaceutical formulations Urine samples	90.8–105 93.3–106	[121]
Rosuvastatin calcium	SWV	CPT-BDDE	1.40	9.40–88.8 μM	1.04 μM (LOD)	0.1 M H_2SO_4	Serum samples Urine samples	98.0–99.0 93.0–109.0	[122]
Amlodipine besylate Hydrochlorothiazide	SWV	CPT-BDDE	0.88 1.30	0.200–9.09 μM 4.00–100 μM	60 nM (LOD) 2.0 μM (LOD)	pH 2.0 BRB	Urine samples	91.0–107.0	[123]
Ticlopidine	DPV SWV	CPT-BDDE	0.96	3.9–38.4 μM	0.66 μM (LOD) 0.84 μM (LOD)	pH 5.0 BRB	Pharmaceutical formulations Urine samples	–	[124]
Imatinib	DPV	APT-BDDE	1.10	0.03–0.25 μM	6.3 nM (LOD) 21 nM (LOD)	pH 2 BRB	Urine samples	102.2–105.5	[125]
Paracetamol Caffeine	DPV	Bi-Nafion-BDDE	0.78 1.44	0.2–500 μM 0.01–20 μM	0.036 μM (LOD) 0.0028 μM (LOD)	0.1 M H_2SO_4	Pharmaceutical formulations	–	[126]
Dopamine Pyridoxine	DPV	PBDDE	0.124 0.66	0.1–700 μM 2.0–1000 μM	0.06 μM (LOD) 0.21 μM (LOD)	pH 7 PBS	Serum samples	96.3–109.4 90.0–109.2	[127]
Tadalafil	SWV	CPT-BDDE	0.905	0.15–1.28 μM	19.5 nM (LOD)	pH 4 BRB	Pharmaceutical formulations	–	[128]
Enrofloxacin	SWV	APT-BDDE	1.27	0.0696–2.78 μM	15.9 nM (LOD)	0.1 M HNO_3	Spiked urine samples	99.04–106.76	[129]
Methotrexate	DPV	APT-BDDE	1.0	0.05–20 μM	10 nM (LOD)	0.05 M H_2SO_4	Pharmaceutical formulations Spiked urine samples	99.2 101.4	[130]
Salbutamol	SWASV	CPT-BDDE	0.95	17.3 μM–0.347 mM	5.06 μM (LOD)	pH 9 BRB	Pharmaceutical formulations	91.8–94.2	[131]
Clopidogrel bisulfate	SWV	CPT-BDDE	1.15	0.60–60.0 μM	0.60 μM (LOD)	pH 5 BRB	Pharmaceutical formulations Urine samples	96.3–104.0 96.7	[132]
Paracetamol	DPV	BDDE B-CNW	0.47	0.065–32 μM 0.032–32 μM	0.430 μM (LOD) 0.281 μM (LOD)	pH 7 BRB	Artificial urine samples	–	[133]
Albendazole	CV-Flow Injection Procedure	BDD film electrode	0.95	3.3–150 ppm	2 ppm (LOD)	0.1 M pH 2.5 PBS	Pharmaceutical formulations	99.4–100.0 99.6–101.8	[134]
6-Mercaptopurine	DPV	APT-BDDE	0.25–1.19–1.63	1–450 μM	0.51 μM (LOD)	pH 2 BRB	Spike urine samples	95.9–101.8	[135]
Amlodipine besylate Ramipril	DPV-SWV	CPT-BDDE	0.68 1.70	0.99–14 μM 0.29–1.9 μM	0.26 μM (LOD) 0.08 μM (LOD)	pH 6 BRB	Pharmaceutical formulations Rat blood samples	92.2–120.7 94.7–101.6	[136]
Chlorpromazine	SWV	nZVI-BDDE	0.63–0.677	0.1–8.0 μM	0.005 μM (LOD)	20 mM pH 7.4 PBS	Pharmaceutical formulations Serum samples	98.6–102.7 97.0–99.5	[137]
Methimazole	SWV	APT-BDDE	0.89	0.5–25.0 μg mL^{-1}	0.085 μg mL^{-1} (LOD)	pH 5 BRB	Pharmaceutical formulations	97.8	[138]
Pindolol	DPV-SWV	CPT-BDDE	0.75	0.04–10.0 μM 0.08–10.0 μM	26 nM (LOD) 43 nM (LOD)	0.2 M pH 6 PBS	Urine samples Serum samples	90.9–96.3 92.6–97.0	[139]

(*continued*)

Table 2. Continued.

Active compound	Method	Electrode	Potential of Peak (V)	Linear range	LOD/LOQ	Buffer or media	Application	Recovery (%)	References
Epinephrine	SWV	APT-BDDE	0.91	1.0–100.0 μM	0.27 μM (LOD)	pH 2 BRB	Pharmaceutical formulations	90.8–104.7	[140]
Lidocaine			1.67	0.1–20.0 μM	0.03 μM (LOD)			92.0–103.0	
Pravastatin	SWV	APT-BDDE	1.328	1.08–16.4 μM	0.204 μM (LOD)	pH 4 PBS	Urine samples	99.0–104.4	[141]
Acetylsalicylic acid			1.932	3.96–42.75 μM	0.078 μM (LOD)				

SWV, square-wave voltammetry; DPV, differential pulse voltammetry; SWASV, square-wave adsorptive stripping voltammetry; LSV, linear sweep voltammetry; BDDE, boron-doped diamond electrode; BDNDE, boron-doped nanocrystalline diamond thin film electrodes; Ni-BDDE, nickel modified boron-doped diamond electrode; BDD NWsE, boron-doped diamond nano-wires electrodes; BDDFE, boron-doped diamond film electrodes; BRB, Britton–Robinson buffer; PBS, phosphate buffer solution; HT, hydrogen-terminated; NEAs, nanoelectrode arrays; AgNP, silver nanoparticle; B-CNW, boron-doped carbon nanowalls; nZVI, nanoscale zero-valent iron.

fabrication of integrated biosensor requires surface activation procedures. Hamers used photochemical methods to introduce a homogeneous layer of amine group on diamond, which serves as binding sites for DNA attachment. The DNA-modified diamond substrates were shown to be highly selective and robust in subsequent hybridization processes.[24]

Nantaphol et al. reported silver nanoparticle-modified BDDE (AgNP-BDDE) for cholesterol detection (Figure 5). The amperometric results showed peak −0.71 (vs. Ag/AgCl) for cholesterol. Under optimized experimental conditions, the amperometric response of modified BDDE gave a good linearity (0.39 mg dL^{-1} to 270.7 mg dL^{-1}), low detection limit (0.25 mg dL^{-1}), high sensitivity (49.61 $\mu A\, mM^{-1}\, cm^{-2}$), the relative standard deviation of 3.76% for 1 mM H_2O_2, and reproducibility of 37.6 mg dL^{-1} cholesterol. Moreover, the developed electrode exhibited between 97.0% and 99.5% recovery of cholesterol in bovine serum analysis. Finally, the proposed voltammetric procedure was successfully applied in the determination of cholesterol in biological samples.[120]

In another approach, Pınar et al. developed a voltammetric sensor for the detection of epinephrine (EP) and lidocaine (LID) based on anodically pretreated BDDE (Figure 6). In this study, SWV was successfully applied to detect epinephrine and lidocaine in pharmaceutical formulations with satisfactory recoveries of 90.8–104.7% and 92.0–103.0%, respectively. The linear range values were found as 1.0–100 and 0.1–20.0 μM. The limits of detection were 0.27 and 0.03 μM under optimized conditions. Good data were obtained with RSD lower than 8.0%. The resulting fit of the calibration plot shows a good correlation with R^2 of 0.998–0.996 and the buffer is Britton–Robinson, pH = 2.0. The simply anodically pretreated non-modified BDD electrode was stable for of 5 days. Moreover, the proposed voltammetric method for simultaneous determination of EP and LID in real samples can be easily and conveniently adopted for routine analysis.[140]

In a recent study, Djebbi et al. carried out the chemical modification of BDDE with nanocomposite of nanoscale zero-valent iron (nZVI) and layered double hydroxide (LDH), which was used as electrochemical sensor for the determination of chlorpromazine in pharmaceutical formulation and human serum samples. The electrochemical properties of the nZVI@LDH/BDDE were investigated by CV and electrochemical impedance spectrometry. Limit of detection was 0.005 μM and linear range was 0.1–8.0 μM by SWV, respectively. The developed nZVI@LDH/BDDE was successfully applied for the detection of chlorpromazine in pharmaceutical formulation and human serum samples. This study showed recoveries from 97.0% to 99.5% and RSD of 3.17%. The proposed method was successfully applied for the chlorpromazine quantification in the pharmaceutical formulations and real samples with acceptable recoveries.[137]

Conclusion

BDDE has superior physical, chemical, and electrical properties such as large potential window, great stability in extreme conditions and low background current that makes it an advantageous choice for electroanalytical studies.[4]

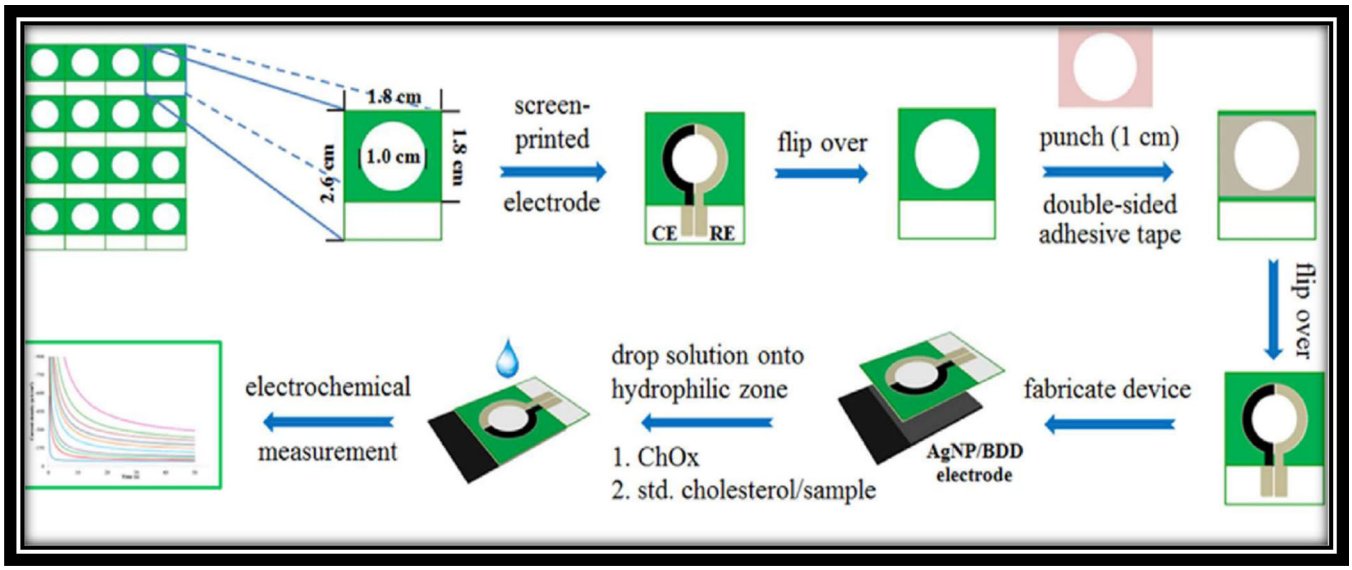


Figure 5. Schematic representation of the fabrication and analytical procedure for the cholesterol sensor based on the coupling of paper-based analytical device (PAD) with AgNP-BDDE. Reprinted from Ref. [121] with permission from Elsevier.

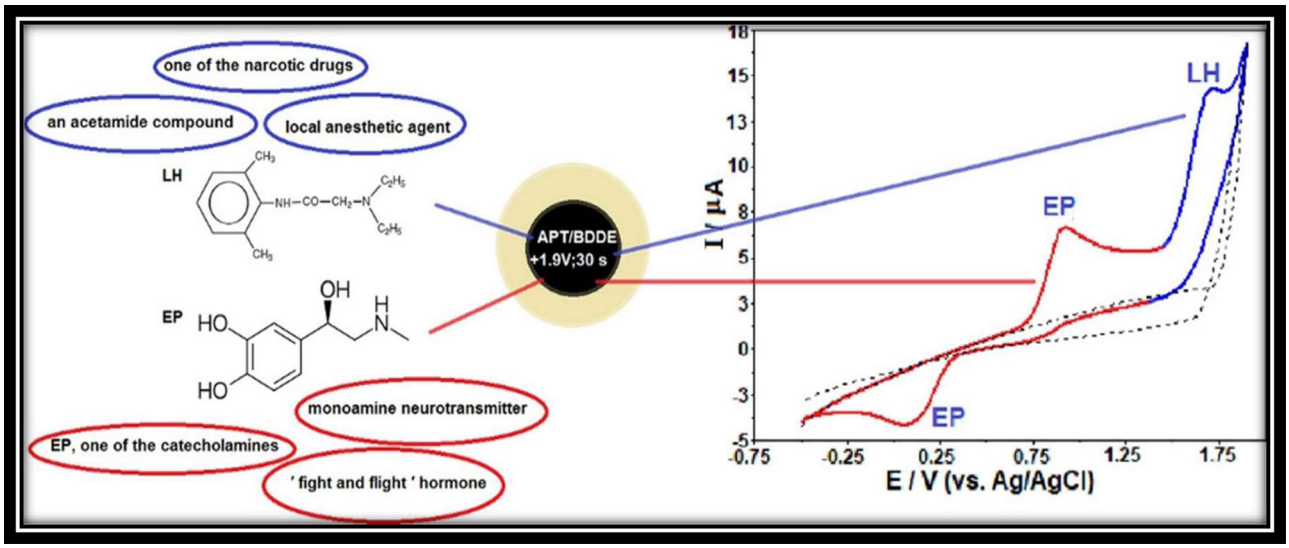


Figure 6. The cyclic voltammogram of mixture solution of LID and EP using anodic pretreatment boron-doped diamond electrode. Reprinted from Ref. [141] with permission from Elsevier.

As described above, BDD films have gained attention in electrochemical fields. Many research papers are published about electrochemical BDD sensors in different fields. Due to complete C-sp^3 hybridization, strong, and covalent tetrahedral bonding of diamond, it provides some desirable properties especially regarding the above-given points. The properties of BDD films are changed with doping by boron. When the doping concentration of the electrode increases, electrical resistivity of it decreases. HPHT and CVD methods are the main growth techniques that are used for the synthesis of doped diamond materials. Electrochemical responses of many redox species are related the fact whether the surfaces of the BDDE are a predominantly hydrogen- or oxygen-terminated. In this review, detailed information on the chemical features, advantages, preparation, and pretreatment of BDDE were explained comprehensively in order to provide an elaborate source for the further studies on BDDE.

Besides, selected novel voltammetric and amperometric studies that were performed for many drug compounds were summarized. Specialized elecroanalytical studies using voltammetric methods at BDD electrodes under optimized conditions are categorized in tables based on method, potential, linear range, LOD, buffer media, application, and recovery.

Additionally, as a relatively new electrode material, BDD needs more attention and further researches about potential applications especially in electroanalytical studies. In addition to already known unique properties, further studies can reveal new advantageous features over other carbon-based electrodes or new applications of current features.

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