Boron Doped Diamond Electrodes in Voltammetry: New Designs and Applications. An Overview

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Abstract: In this overview, the recent progress in the development and applications of bare boron doped diamond electrodes in voltammetry of organic compounds is summarized. Attention is paid to important issues reflected in last five years in electroanalytical studies, *e.g.* fouling and pretreatment of BDD surface, influence of boron concentration on performance of BDD-based sensors, and application of adsorptive stripping voltammetry.

Keywords: Boron doped diamond electrode; Organic compounds; Voltammetry; Review

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Introduction

Boron doped diamond (BDD) is a versatile electrode material, which has gained deserved popularity in a variety of electrochemical applications since its introduction in 1992 [1-3]. It is substantiated by its excellent mechanical, physical, and electrochemical properties, such as extreme hardness, very low and stable capacitive background current over a wide potential range, microstructural stability at extreme cathodic and anodic potentials, electrochemical stability in both alkaline and acidic media, good responsiveness for many redox analytes without pretreatment, and resistance to electrode fouling. Four main application ways

established during the twenty year history of BDD-related research: (i) Electrochemical oxidation of environmental pollutants at BDD anodes proposed for their quantitative conversion or destruction in wastewaters, (ii) electrochemical disinfection of drinking and bathing water, (iii) use of BDD electrodes in electroanalysis for detection of organic and inorganic species in environmental, biological and pharmaceutical matrices, (iv) developing of BDD-based sensors and biosensors, and (v) electrochemical synthesis, in particular in the production of strong inorganic oxidizing agents, or in electroorganic synthesis [4].

The properties of BDD films are fundamentally influenced by the quantity and kind of the doping agent, morphologic factors and defects in the film, presence of impurities (sp^2 carbon), crystallographic orientation, and surface termination (most frequently oxygen or hydrogen). While the former factors are given by the preparation method, the latter can be determined by post-preparation procedures including electrochemical pretreatment.

The preparation of doped diamond films relies on energy-assisted chemical vapor deposition (CVD) methods, when a carbon containing gas, most frequently methane is energetically activated to decompose the molecules into methyl-radicals and atomic hydrogen and deposited on a suitable substrate. The boron doping agent is most frequently added as small amounts of diborane or trimethyl boron in the gas phase. The gas activation is accomplished using microwave plasma (MP CVD) or hot filament (HF CVD) techniques. Typical growth conditions are: 0.3-1.0 % CH_4 in H_2, pressures of 10-150 torr, substrate temperatures of 700-1000 °C, and microwave powers of 1000-1300 W, or filament temperatures up to ~ 2800 °C, depending on the methods used. The film grows by nucleation at rates in the 0.1-2 µm h^{-1} range. For the substrates to be continuously coated with diamond, the nominal film thickness must be ~ 1 μm. The resulting films differ in morphology − microcrystalline films are characterized by crystallite size < 1-5 µm, nanocrystalline films 10-500 nm [5] − and quality. It is generally accepted, that the quality of MP CVD films, *i.e.* content of sp^2 impurities and structure defects is enhanced compared with HF CVD film.

The as-deposited diamond surface is hydrogen-terminated, because the films are grown under hydrogen plasma or in a hydrogen atmosphere. Such hydrogen-terminated diamond surfaces are known to be remarkably stable, but the oxygen-terminated surface can easily be formed by exposing the surface to oxygen plasma, boiling in strong acid or electrochemical exposure to the high anodic potential in the region of water decomposition. The change of the chemical termination affects the electrochemical properties of the diamond electrode. The water decomposition reaction is extremely important for the application fields (i-iii) listed above. At BDD electrode, water decomposes according to the following equation:

$$H_2O(BDD) \rightarrow HO^{\bullet}(BDD) + H^+ + e^- \qquad\qquad (\ 1\ )$$
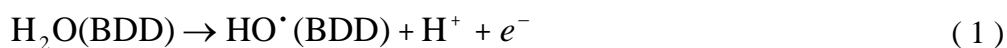
The $OH^{\bullet}$ radicals are confined to the BDD surface and as powerful oxidizing agents are capable of oxidation of a wide range of compounds, non-oxidizable using other electrode materials. Reaction (1) is enabled by the high oxygen overvoltage at BDD surface.

This overview is based on findings gained by going through the papers devoted to the use of BDD electrodes in voltammetric analysis and personal experience of the authors and their coworkers. Table I summarizes selected examples of organic compounds investigated since 2008 by means of batch voltammetric methods using bare BDD electrodes. The table contains for each analyte electroanalytical method, characterization of used BDD electrode, achieved limit of detection (LOD), eventually matrix, and thus enables an insight in the progress in application of BDD electrodes in last five years.

Applications of BDD Electrodes in Voltammetry

Organic compounds can be oxidized on BDD electrodes by two basic mechanisms: (i) directly by electron transfer from BDD surface to compound, or (ii) in indirect way by oxidizing entities, *e.g.* hydroxyl radicals, generated on electrode surface by reaction (1). The latter mechanism is unique for BDD electrodes and enables oxidation of organic compounds at far positive potentials, non-achievable at other electrode materials in aqueous or mixed aqueous-organic media. Methods based on reductive determinations are still not that frequent. Nevertheless, they benefit from the low sensitivity of BDD surface to dissolved oxygen that is being recognized in increasing number of publications [6, 7].

In the following paragraphs, the selected factors and approaches influencing the development of batch voltammetric methods by means of planar bare BDD electrodes are briefly analyzed and demonstrated on examples mostly coming from experimental work of the authors and coworkers.

Table I: *Selected applications of bare BDD electrodes in voltammetric determination of organic analysis.*

Analyte	BDD electrode, pretreatment[a]	Method (matrix[B])	LOD[A] [μmol L^{-1}]	Ref.
Phenolic Compounds				
Benzophenon-3	HFCVD BDD[b], AT at +3.2 V, CT at −2.8 V (30 s) in 0.1 mol L^{-1} HClO$_4$	SWV[c]	0.14[d, C]	[23]
Bisphenol A	Commercial BDD [28], CT at −250 mA cm^{-2} (180 s)	DPV	0.21	[29]
Nitrophenols and Other Nitroaromatics				
4-Nitrophenol	Commercial BDD [30], oxidation by repeated cycling between −2.5 V and	DPV (river water)	[F]1[e], 0.1[d]	[6]
2,4-Dinitrophenol	+2.5 V in 1 mol L^{-1} HNO$_3$		0.3[e], 0.6[d]	
2-Nitrophenol			0.1[d]	
5-Nitroimidazole	MPCVD microcrystalline BDD, AT at +2.5 V (15 min), before each scan 100 ms pulses at 0 V and +1.7 V for 30 s	DCV, DPV (river water)	0.9, 0.7[d,E]	[16]
Aromatic Hydrocarbons and Their Amino-, Nitro-, and Hydroxy Derivatives				
Benzo[a]pyrene	Commercial polished BDD [30], manual polishing by Al$_2$O$_3$ slurry followed by AT at +1.3 V (30 s)	AdSSWV[f] (tap water)	0.0102	[22]
1-, 2-Naphthylamine	MPCVD microcrystalline BDD, AT at +2.4 V (60 s) in 0.1 mol L^{-1} HNO$_3$	DPV	0.89, 0.44[E]	[31]
1-Aminopyrene	Commercial polished BDD [30]	DPV	0.06	[32]
1-Nitropyrene			0.3	
1-Hydroxypyrene			0.1	
Aminonitrophenols	Commercial BDD [28], CT at −3.0 (10 s) followed by AT at +3.0 V (10 s) in 1 M HNO$_3$	DPV	0.4–0.9[e] 0.2–0.6[d]	[33]

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Analyte	BDD electrode, pretreatment [a]	Method (matrix [B])	LOD [A] [μmol L^{-1}]	Ref.
Agrochemicals				
Carbendazime, Fenamiphos	Commercial BDD [28], AT at +3.0 (10 min) followed by CT at −3.0 V (10 min) in 0.5 mol L^{-1} H$_2$SO$_4$	SWV	0.12 [C] 0.10	[34]
Dichloran	MPCVD microcrystalline BDD, oxidation as in [6]	DPV LSV	0.5 [d,E] 1.9 [d,E]	[35]
Methyl parathion	Commercial BDD [28], AT at +3.0 (1 s) followed by CT at −3.0 V (30 s) in 0.5 mol L^{-1} H$_2$SO$_4$	Sono-SWV	0.019 [d,C]	[36]
Pharmaceuticals				
Acetylsalicylic acid	HFCVD BDD [b], AT at +1.0 V (60 s) followed by CT at −1.0 V(120 s) in 0.5 mol L^{-1} H$_2$SO$_4$	SWV	2 [C]	[37]
Bezafibrate	HFCVD BDD (8000 ppm, [28]), AT at i =+0.5 mA cm^{-2} (20 s) followed by CT at i =−0.5 mA cm^{-2} (80 s) in 0.5 mol L^{-1} H$_2$SO$_4$	DPV	0.098	[38]
Brimonidine	Commercial BDD [30], polishing by Al$_2$O$_3$ slurry AT at +1.2 V (60 s), CT at −1.5 V (60 s) in 0.25 mol L^{-1} H$_2$SO$_4$	DPV SWV	0.64 [d,G] 0.13 [d,G]	[7]
Caffeine Acetylic acid [g]	HFCVD BDD [b], CT in 0.5 mol L^{-1} H$_2$SO$_4$ at −9 C cm^{-2}, AT in 0.5 mol L^{-1} H$_2$SO$_4$ at +5 C cm^{-2}	DPV	0.16 0.23	[39]
Caffeine Paracetamol [g]	HFCVD BDD [b], CT in 0.5 mol L^{-1} H$_2$SO$_4$ 180 s at i =−1.0 A cm^{-2} (180 s)	DPV	0.49 0.035	[40]
Chloramphenicol	MPCVD microcrystalline BDD, oxidation as in [6], stirring between individual scans	DCV DPV	3 [d,H] 3	[41]
Codeine	Commercial BDD [30], 1000 ppm, AT by CV from −2 V to +2 V (10 min) in 0.1 mol L^{-1} HNO$_3$	DPV	0.08 [C]	[42]
Penicillin V	Commercial BDD [30], no pretreatment	DPV	0.5-40 [C]	[43]

Analyte	BDD electrode, pretreatment [a]	Method (matrix [B])	LOD [A] [μmol L⁻¹]	Ref.
Penicillin V, Paracetamol [g]	Commercial BDD [30], no pretreatment	SWV	0.21 / 0.32	[44]
Lornoxicam	Commercial BDD [30], polishing by Al$_2$O$_3$ slurry before each scan	SWV (plasma) / DPV	0.16 (0.037) / 0.17 [F]	[45]
Ofloxacin	MPCVD microcrystalline BDD, oxidation as in [6], stirring between individual scans	DCV / DPV	0.4 [H] / 1	[41]
Quinine	MPCVD microcrystalline O-BDD, stirring between individual scans	DPV	1.3 [e] / 43.3 [d]	[46]
Quinizarin	BDD, manual polishing by Al$_2$O$_3$ slurry and sonication for 1 min before each scan	CV	0.2 [d,I] / 0.005 [h,I]	[47, 48]
Sertindole	Commercial BDD [30], manual polishing by Al$_2$O$_3$ slurry before each scan	SWV (plasma) / DPV (plasma)	0.22 (0.25) [E] / 0.24 (0.25)	[49]
Sildenafil	HFCVD BDD [b], CT in 0.5 mol L⁻¹ H$_2$SO$_4$ (240 s) at i = +1.0 A cm⁻²	DPV	6.4 [C]	[50]
Sulfamethoxazole	HFCVD BDD [b], CT at i = −0.5 mA cm⁻² (60 s) in 0.5 mol L⁻¹ H$_2$SO$_4$	DPV	0.014,0.0135	[51]
Trimethoprim		DPV [i]	0.065,0.063 [C]	[52]
6-Thioguanine	Commercial BDD [30], pretreatment by CV as in [6]	DCV, DPV	0.6, 0.6 [F]	[53]
Zolmitriptan	Commercial BDD [30], manual polishing by Al$_2$O$_3$ slurry before each scan	DPV (plasma) / SWV	0.073 (0.294) / 0.263 [E]	[54]
Food Components and Additives				
BHA	Commercial HFCVD BDD [28], CT at −1 A cm⁻² V (120 s) in 0.5 mol L⁻¹ H$_2$SO$_4$	SWV	0.14 [C]	[55]
BHT			0.25	
Capsaicin	Commercial polished BDD [30], manual polishing by Al$_2$O$_3$ slurry	AdSSWV [f]	0.034 [C]	[21]
Chlorogenic acid	Commercial polished BDD [30], manual polishing by Al$_2$O$_3$ slurry	AdTSSWV	0.049 [C]	[20]

Analyte	BDD electrode, pretreatment [a]	Method (matrix[B])	LOD[A] [μmol L⁻¹]	Ref.
Other Compounds				
Glucose[j]	n-Si (111)/ HF CVD BDD, used as deposited	LSV	25	[56] [57]
Glycerol	Commercial polished BDD [30]	CV, DPV / SWV	149, 356 / 1100	[58]
Oxalic acid	Commercial polished BDD [30], oxidation by three repetitive cycling between −0.5 V to +1.75 V in 0.1 mol L⁻¹ Na₂SO₄	DPV	Not given	[59]
Estriol	HFCVD BDD[b], CT in 0.5 mol L⁻¹ H₂SO₄ for 30 min at −3 V, CT for 30 s in measured solution at −3 V prior to each scan	SWV	0.17[J]	[60]
Indole-3-acetic acid	Commercial BDD [30], AT in 0.5 mol L⁻¹ H₂SO₄ for 30 s at +3 V, AT for 30 s in measured solution at +3 V prior to each scan	SWV	1.22[F]	[61]

Legend: AdSSWV – adsorptive stripping – square wave voltammetry; AdTSSWV – adsorptive transfer stripping – square wave voltammetry; AT –anodic treatment; BHA - butylated hydroxyanisole; BHT - butylated hydroxytoluene; CT – cathodic treatment; CVD – chemical vapor deposition; CV – cyclic voltammetry; DPV – differential pulse voltammetry; LSV – linear sweep voltammetry; SDS – sodium dodecylsulfate; SWV – square wave voltammetry.

[a] if no details are given, as deposited polycrystalline H-terminated electrodes and undefined silica support used; [b] polycrystalline BDD from CSEM, B/C ratio 8000 ppm; [c] in the presence of CTAB; [d] reductive determination; [e] oxidative determination; [f] in the presence of SDS; [g] simultaneous voltammetric determination; [h] quanizarine-mediated oxygen reduction; [i] in stopped flow system with thin-layer cell; [j] in the presence of ascorbic and uric acid.

[A] LOD for $S/N = 3$, if not otherwise specified; [B] if no matrix given, listed LODs are for model experiments in solutions prepared with deionized water; [C] $LOD = 3s_b/m$, and [D] $LOQ = 10s_b/m$ where s_b is the standard deviation of the mean of the current at the peak potential for repeated voltammograms of the blank solution, m is slope of the calibration curve; [E] $LOD = 3\sigma/m$, [F] $LOQ = 10\sigma/m$ where σ is the standard deviation of the signal measured for the lowest analyte concentration corresponding to calibration plot, m is slope of the analytical curve; [G] $LOD = 3s_i/m$ where s_i is standard deviation of the intercept and m is slope of the calibration curve; [H] LOQ calculated using statistic software ADSTAT version 2.0 (Trilobyte, Czech Republic). This software uses confidence bands (α = 0.05) for calculation of the LOQ. It corresponds to the lowest signal for which relative standard deviation RSD is equal 0.1; [I] the lowest measured concentration; [J] $LOD = 2s_i/m$, explanation as for [G].

Fouling of the BDD Surface

Initially, BDD electrodes have been considered as resistant to fouling due to the paraffin-like, hydrogen terminated surface [8]. Nevertheless, it has been clearly proven that this is not a general rule and a number of studies demonstrated fouling problems. Formation of polymeric film on the electrode surface causes rapid deactivation of electrode by blocking electron transfer and slowing down further oxidation. Choosing appropriate solvents and supporting electrolyte systems and electrochemical pretreatment of the electrode may be an alternative option for the reactivation of the electrode surface. An example of electrode fouling in the presence of 2-aminobiphenyl and remediation of the surface using anodic and cathodic pretreatment is given in Fig. 1 [9]. Beside aromatic amines (*e.g.*, metoclopramide [10]), also phenolic compounds (*e.g.*, ref. [11]) are susceptible of causing BDD passivation, because both compounds produce reactive radicals (phenoxy radicals or amino cation radicals) capable of further dimerization and polymerization at the electrode surface. The strategies to prevent passivation are discussed below.

Pretreatment of the BDD Surface

Pretreatment of the electrode surface can be applied for conditioning of the electrode surface, enhancement of the voltammetric signals, preventing the passivation of electrode surface, and ensuring of repeatable and reproducible response of particular analytes. The basic strategy for conditioning of the electrode surface is its electrochemical anodic oxidation ($\sim \theta +2.0$ V) for minutes in the region of water decomposition. The formation of OH radicals (Eq. 1) causes oxidation and stabilization of the electrode surface with the prevalence of the ketonic, alcoholic and carboxylic groups [12]. While at the beginnings many studies were presented to be performed at as grown, H-terminated BDD surfaces, this approach is superannuated nova days because the maintenance of H-termination is complicated due to the easy of electrochemical oxidation and even oxidation of BDD surface by air oxygen [13]. The re-hydrogenation of an oxidized BDD surface is achievable only by hydrogen-flame annealing or hydrogen-plasma treatment, which requires adequate equipment. It can be presumed that many of the early studies performed using allegedly H-terminated surfaces were in fact conducted at oxidized BDD surfaces.

Further optimization of electrode pretreatment has to result in experimental protocol ensuring possibly repeatable, maximized, and well evaluable signals. For this purpose, most frequently high positive/negative current densities or potentials (~ θ ±2.0 V) applied for few seconds to minutes are used. As results of this anodic/cathodic pretreatment, oxygen-terminated (O-BDD) or hydrogen-terminated (H-BDD) surfaces are produced. The importance of cathodic pretreatment was called by Suffredini *et al.*, who presented faster electron transfer for $[Fe(CN)_6]^{4-/3-}$ and signal increase and improved repeatability for selected chlorophenols [14]. The cathodic pretreatment has to be applied just before the electrochemical experiments to ensure reliable and reproducible results, especially when the electrode has not been used for a long period of time due to its instability in air [15]. It facilitates the interaction and adsorption of the electrochemical species with the electrode surface and thus clearly leads to a larger electrochemical activity for a number of compounds, as can be traced in Table I.

Anodic pretreatment before each scan is a powerful tool for preventing electrode fouling, as demonstrated at Fig. 1C for 2-aminobiphenyl. The peak height repeatability characterized by relative standard deviation is 2.7 %, and anodic pretreatment is thus favorable compared with cathodic pretreatment, leading to instability of voltammetric responses (Fig. 1B).
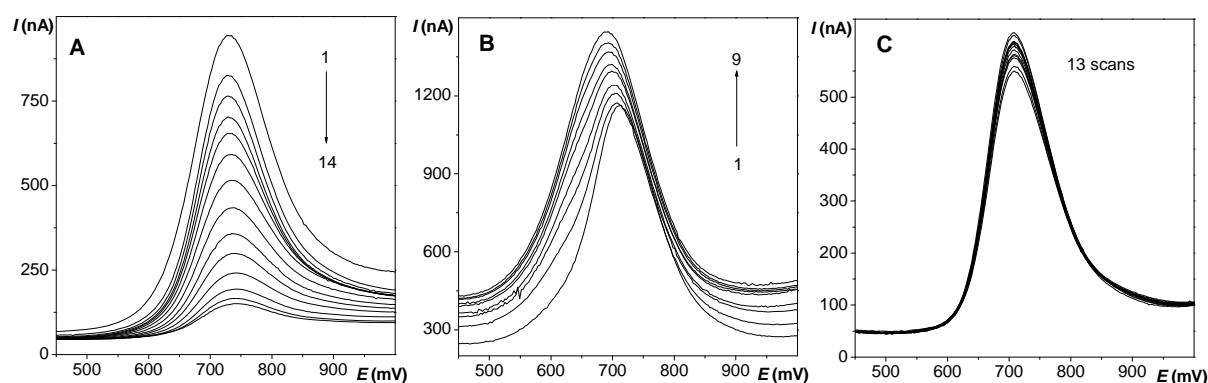

Fig. 1: *Influence of the electrode pretreatment on the differential pulse voltammograms of 2-aminobiphenyl (c = 5·10^{-5} mol dm^{-3}) in BR buffer pH 7.0.* Measured on BDD without pretreatment (A) and with pretreatment consisting of stirring and applying the potential of –2.4 V (B) or +2.4 V (C) for 15 s on working electrode in measured solution between individual measurements. The number of scans is indicated in particular figures.

Other option of electrode activation includes application of cyclic voltammetry, mostly in acidic media, or repeated application of short potential pulses close or in the onset of supporting electrolyte curve. Examples of these approaches include determination of 5-nitroimidazole (basic structural unit of some antibiotics) in model samples of drinking water (see ref. [16] and fig. 2 therein).
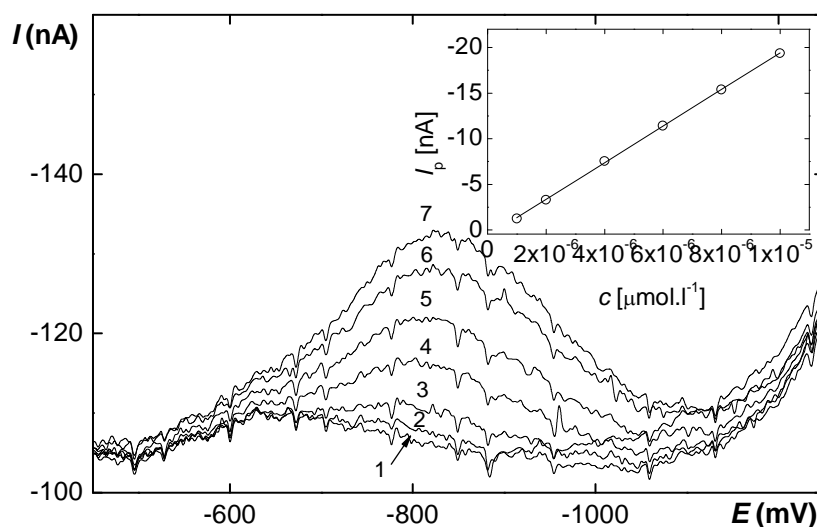

Fig. 2: *Differential pulse voltammograms of 5-nitroimidazole in model samples of river water (river water – acetate buffer pH 4.6 (9:1)).* Concentration c of 5-nitroimidazole: 0 (1); $1 \cdot 10^{-6}$ (2); $2 \cdot 10^{-6}$ (3); $4 \cdot 10^{-6}$ (4); $6 \cdot 10^{-6}$ (5); $8 \cdot 10^{-6}$ (6) a $10 \cdot 10^{-6}$ (7) mol l^{-1}. Measured on BDD with pretreatment consisting of stirring and applying 100 ms lasting potential regeneration pulses $E_{reg,1} = 0$ V, $E_{reg,2} = 1.7$ V for 30 s on working electrode in measured solution between individual measurements. Inset corresponding calibration dependence. Reproduced from [16].

Boron Concentration

The concentration of boron influences significantly the electrochemical properties of the BDD films. It is usually given as B/C ratio in the gas phase during the CVD process and films deposited at B/C ratio 100 – 10000 ppm corresponding to final boron concentration in the film [B] $\sim 1.10^{19}$ cm^{-3} − 1.10^{21} cm^{-3} were tested in last years. Obviously, increased boron content leads to higher capacitance, slightly narrower solvent windows and can increase the likelihood of undesirable incorporation of sp^2 impurities. Depending on the doping level, BDD films present either semiconducting or metallic electronic properties, with boundary

boron content of about $1\text{-}3.10^{20}$ cm^{-3} (ref. [13, 17]). These concentrations are sufficient to achieve fast electron transfer. Despite the fact that increased interest may be traced in last five years on this problematic and the information on boron doping level is frequently present in electroanalytical publications, only few studies address its influence on electroanalytical characteristics including the width of the potential window [13, 17] or on sensitivity for particular analytes including *e.g.* the floroquinolone enrofloxacin [18] or our results for 2-aminobiphenyl [19].

Adsorptive Stripping Voltammetry

Bare BDD surfaces have been considered for a long period as relatively inert to the adsorption for organic compounds, nevertheless a few examples on the use anodic adsorptive stripping voltammetry for oxidizable compounds have been reported in last five years. These include utilization of the adsorption of the analyte itself or the absorption of surfactants interacting with organic analytes on the BDD surface. The former approach enabled determination of antioxidant capacity in the coffee samples based on the oxidation peaks of present phenolic compounds – chlorogenic, caffeic, and gallic using adsorptive transfer stripping voltammetry [20]. The interaction of surfactant and an organic compound can change the redox potential, charge transfer coefficient or diffusion coefficient of the electrode processes and thus leads to improved analytical figures of merit as presented for detection of capsaicin [21] or benzo(*a*)pyrene [22] in the presence of sodium dodecylsulfate or benzophenone-3 in the presence of cetyltrimethylammonium bromide (CTAB) [23]. The main disadvantage of this approach is the necessity of manual polishing of the BDD surface after each scan. On the other hand, the interaction of the surfactant or transfer of the adsorbed species from the matrix to pure supporting electrolytes can substantially increase the selectivity of the method.

BDD-Based Electrodes and Sensors

Beside the classical planar nanocrystalline and microcrystalline BDD films deposited at silica, eventually tungsten, numerous attempts were made to design BDD-based microelectrodes, BDD microdisc arrays or other variations (summarized in review [24]). Regardless on the miniaturization trend, benefits of increase of active electrode area and roughness of the

surface were demonstrated in detection of dopamine and non-enzymatic amperometric detection of glucose [25] using 3D-structured BDD nanorod forest electrode. Conductive BDD powder and polyester binder were used to fabricate screen-printed electrode on polyimide sheets and exhibited greater durability to fouling by dopamine than carbon screen-printed electrode [26]. Further, many studies exist on modified BDD surfaces and their utilizations in construction of BDD-based sensors (for details, see [2, 27]). Further development in this field can be foreseen thanks to the progress in the deposition technology of the BDD films, their modification and widening insights in the principles of biosensing.

Conclusions

Obviously, the possibilities of BDD electrodes in voltammetric methods hold an unceasing interest, which can be documented by a number of publications demonstrating practical applicability of the developed methods on analysis of various matrices. The most vivid field is presumably their utilization for detection of pharmaceutical substances. Hopefully, further research will supports their expansion in pharmaceutical, clinical and environmental laboratories, so that their advantageous properties enabling versatile use can be appreciated not only in the academic, but more in commercial sphere.

Acknowledgements

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