

Review Article

Electrochemical Biosensor Based on Boron-Doped Diamond Electrodes with Modified Surfaces

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Boron-doped diamond (BDD) thin films, as one kind of electrode materials, are superior to conventional carbon-based materials including carbon paste, porous carbon, glassy carbon (GC), carbon nanotubes in terms of high stability, wide potential window, low background current, and good biocompatibility. Electrochemical biosensor based on BDD electrodes have attracted extensive interests due to the superior properties of BDD electrodes and the merits of biosensors, such as specificity, sensitivity, and fast response. Electrochemical reactions perform at the interface between electrolyte solutions and the electrodes surfaces, so the surface structures and properties of the BDD electrodes are important for electrochemical detection. In this paper, the recent advances of BDD electrodes with different surfaces including nanostructured surface and chemically modified surface, for the construction of various electrochemical biosensors, were described.

1. Introduction

Combining the advantages of the electrochemical techniques, electrochemical biosensors have been increasingly developed for many applications in environmental monitoring, food analysis, detection of biological metabolites, and clinical chemistry, and so forth, due to their specificity, sensitivity, accuracy, and portability [1–3]. The performance of electrochemical biosensors mainly depend on the physical and chemical characteristics of the materials, including shape and structure, employed for the construction of the transducer and the methods used for the immobilization of biomolecules. Conventional carbon-based materials including, carbon paste, porous carbon, glassy carbon, and carbon nanotubes have been widely employed as electrochemical transducers in the field of biosensors due to simple preparation methods, large positive potential ranges, and suitability for chemical modification [4–7]. However, traditional carbon-based electrodes still suffer some drawbacks, such as electrode fouling, which limits their long-term stability and leads to frequent polishing or disposal of the electrode.

Boron-doped diamond (BDD) thin films, as one new kind of electrode materials, are gaining big researching interests. Nowadays, the development of diamond growth by chemical vapor deposition has enabled the preparation of the BDD electrodes with different surface structures on various substrates. The electrochemical properties of the BDD electrodes have also been intensively studied [8–12]. The results showed that the BDD electrodes possess many outstanding properties, including wide electrochemical potential window, low and stable capacitive background current, high response reproducibility and long-term response stability, and good biocompatibility. Therefore, BDD electrodes have been widely employed for the construction of various electrochemical biosensors. It was well known that electrochemical reactions proceed at the interface between electrolyte solutions and electrodes surfaces, so the surface structures and properties of BDD electrodes are important for electrochemical biosensors. The present paper summarizes the biosensors based on BDD electrodes materials with different surfaces, including nanostructured surfaces and chemically modified surface.

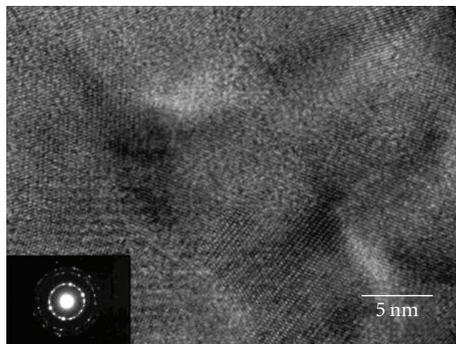


FIGURE 1: TEM image and ED pattern for a boron-doped nanocrystalline diamond thin film.

2. Biosensors Based on BDD Electrodes with Nanostructured Surfaces

Nanostructured materials are considered to be much more efficient and selective than traditional bulk materials for their high surface areas and high surface energy [13, 14]. For example, many carbon-based nanostructured materials have been shown to be ideal for biosensing applications since they are conductive, biocompatible, and easily functionalized and possess very large surface areas [15, 16]. However, the main disadvantage of these carbon-based materials is nonstability of potential, which remains a limiting factor. Therefore, it is of interest to inquire if BDD electrodes with much smaller lateral dimensions can be fabricated, and what properties such electrodes might possess. The methods for fabrication of nanostructured diamond films, such as diamond nanowhiskers and nanorods by microfabrication methods involving RIE (reactive ion etching) or plasma etching on diamond films [17–20], and homoepitaxially grown diamond nanorods by CVD technique using template [21, 22] have been reported. However, conductive nanostructured diamond films used in electro- or biochemistry applications have seldom been reported. Surface modification of the BDD electrodes is necessary to improve their detection performance; however, the ideal characteristics of the BDD electrodes could be lost. Hence, it is critical to create functional BDD films without the loss of favorable properties. This can be realized by creating nanostructured BDD electrodes. Show et al. deposited boron-doped nanocrystalline diamond thin films using CVD method from a $\text{CH}_4/\text{H}_2/\text{Ar}$ source gas mixture [23]. Figure 1 is a TEM image of the BDD film showing that the BDD film consists of 10–15 nm randomly oriented but atomically ordered diamond grains. The films exhibited a wide working potential window, a low voltammetric background current, and good responsiveness for $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{2+/3+}$, $\text{IrCl}_6^{2-/3-}$, and methyl viologen without any pretreatment. It was found to be useful for the detection of trace metal ions, such as Ag(I), Cu(II), Cd(II), Pb(II), and Zn(II).

Luo et al. combined the electroless metal deposition (EMD) and hot filament chemical vapour deposition (HFCVD) technique preparing a BDD nanorod forest

(BDDNF) electrode on silicon nanowires arrays, that is, transforming a planar BDD electrode to a three-dimensional nanostructured BDD electrode (Figures 2(a) and 2(b)) [24]. The BDD nanorod forest was demonstrated as a nonenzymatic glucose biosensor by simply putting it into the glucose solution. The BDD nanorod forest electrode exhibits very attractive electrochemical performance compared to conventional planar BDD electrodes, notably improved sensitivity and selectivity for glucose detection. The limit of detection was estimated at a signal-to-noise ratio of 3 to $0.2 \pm 0.01 \mu\text{M}$. Selective determination of glucose in the presence of AA and UA and high stability were also obtained.

Recently, a novel boron-doped diamond micronetwork (BDDMN) film shown in Figures 2(c) and 2(d) has been successfully prepared by the authors via a photomask microfabrication process coupled with synthesis of silicon nanowires and BDD films [25]. Uric acid (UA) was used to estimate the electrochemical biosensing properties of the BDDMN electrode. Studies of the amperometric response of the BDDMN electrode and the planar BDD electrode were carried out through successive addition of UA in 0.1 M PBS solution under continuously stirring conditions. As shown in Figure 3. The current response of the BDDMN electrode was higher than that of the BDD electrode for the same concentration of UA. Sensitivity for UA was obtained with $21.35 \mu\text{A mM}^{-1}$ on the BDDMN electrode and $6.28 \mu\text{A mM}^{-1}$ on the planar electrode by linearization of the response current on the concentration. This result is ascribed to the network structure that could change the reactive sites, resulting in different adsorption sites and catalytic effect toward the analyte.

A simple method to prepare a BDD nanoglass array on a BDD film by reactive ion etching has been reported [26, 27]. The nanoglass array with $\sim 20 \text{ nm}$ diameter and $\sim 200 \text{ nm}$ length has been formed on the BDD surface after oxygen plasma etching treatment. The effect of the nanoglass array structure on the enhancement of electrocatalytic activity of electrodes was demonstrated by detecting DA and UA. On the BDD nanoglass array electrode, there are two well-defined peaks at 0.38 V and 0.78 V in neutral buffer solution, corresponding to the oxidation of DA and UA. This result is ascribed to the nanoglass array on the BDD surface that could change the reactive sites, resulting in a different adsorption affinity and catalytic effect toward the different substances, thus enhancing the selectivity for some coexisting compounds [26]. The electrochemical behavior of different redox systems and detection of catechol were performed on the as-grown boron-doped diamond (BDD) electrodes and the nanoglass array BDD. Compared with as-grown BDD, the electron transfer on the nanoglass array BDD surface became slower toward the negatively charged $\text{Fe}(\text{CN})_6^{3-}$ whereas changed little toward the positively charged $\text{Ru}(\text{NH}_3)_6^{3+}$. The nanoglass array BDD showed higher electrocatalytic activity toward the catechol detection than did the as-grown BDD. Good linearity was observed for a concentration range from 5 to 100 mM with a sensitivity of $719.71 \text{ mA M}^{-1} \text{ cm}^{-2}$ and a detection limit of 1.3 mM on the nanoglass array BDD [27].

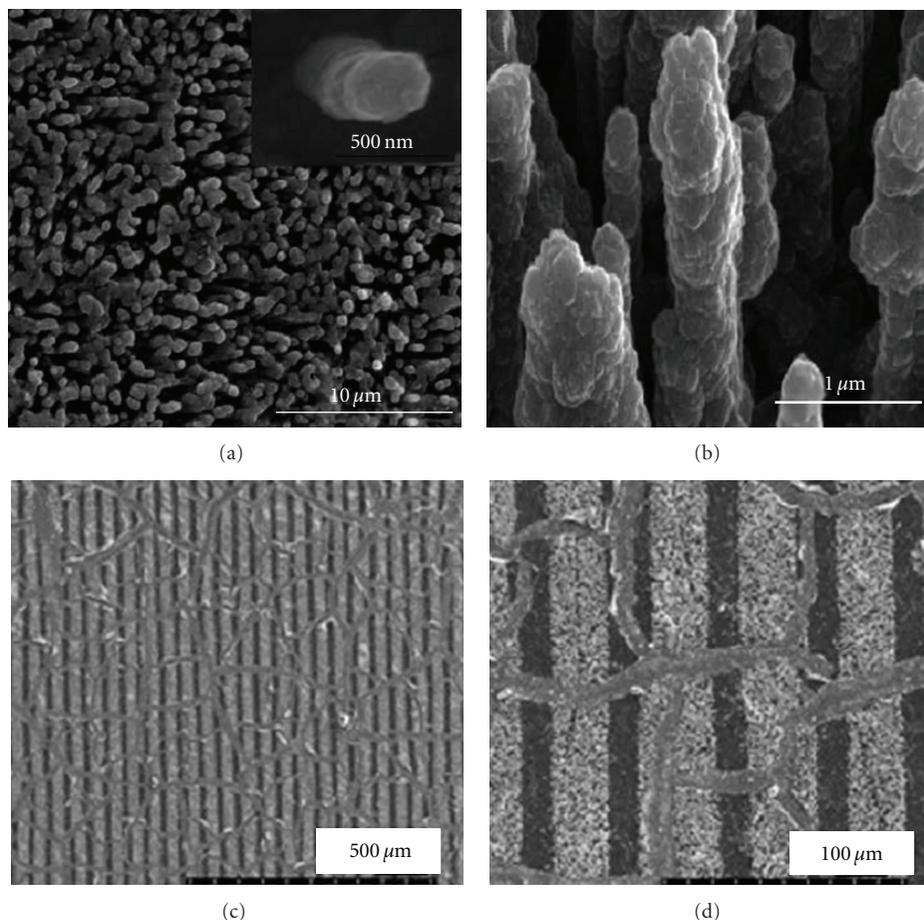


FIGURE 2: Images of BDD films with nanostructured surfaces: (a) and (b) BDD nanorod forest electrode image taken from different magnifications; (c) and (d) 2D micronetwork of boron-doped diamond film taken from different magnifications.

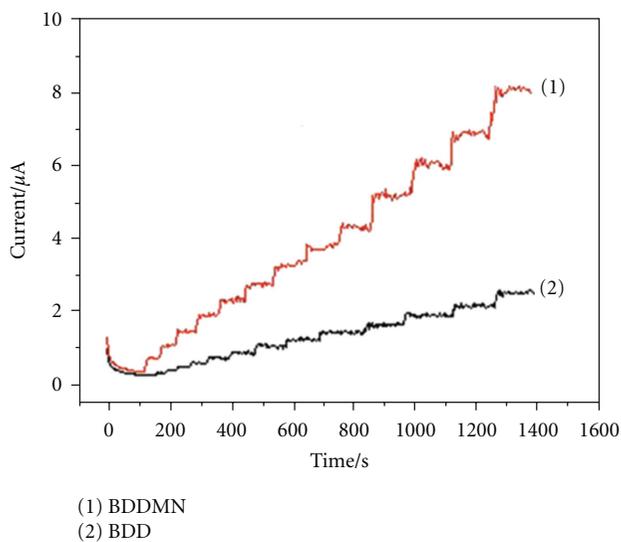


FIGURE 3: Current-time responses of the BDD electrode (1) and the BDDMN electrode (2) through successive addition of UA (each step of the curves indicates 0.013, 0.026, 0.04, 0.052, 0.064, 0.076, 0.088, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, and 0.4 mM from low to high) in 0.1 M PBS solution at an applied potential of 0.4 V (versus SCE, for both electrodes, the oxidation current response occurs at 0.4 V).

The nanostructured BDD electrodes can improve the reactive site, accelerate the electron transfer, promote the electrocatalytic activity, and enhance the selectivity [28]. They not only overcome the disadvantages of the as-grown BDD film electrodes but also avoid the disadvantages associated with surface modification of the electrode. The above excellent properties of these nanostructured BDD electrodes indicate the promise for real biochemical applications.

3. Electrochemical Biosensors Based on Planar BDD Electrodes with Chemically Modified Surface

Electrochemical reactions perform at the interface between electrolyte solutions and the electrodes surfaces, so the surface properties of the BDD electrodes are important for electrochemical detection. The recent advances of BDD electrodes with different surfaces including hydrogen-terminated, oxygen-terminated, metal nanoparticles modified, amine-terminated, and carboxyl-terminated thin films, for the construction of various biosensors or the direct detection of biomolecules were described.

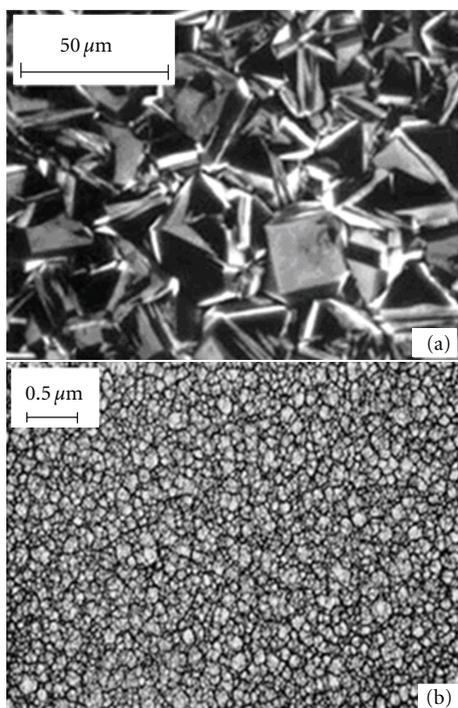


FIGURE 4: SEM images of (a) a polycrystalline BDD thin film and (b) a nanocrystalline BDD thin film.

3.1. Electrochemical Biosensors Based on Hydrogen-Terminated BDD Electrode. The surface of an as-deposited polycrystalline BDD electrode (Figure 4(a)) and nanocrystalline BDD electrode (Figure 4(b)) prepared by chemical vapor deposition using hydrogen gas as carrier gas is recognized to be hydrogen-terminated, and its scanning electron microscopy images is shown in Figure 4(a) [10]. A clean and homogeneous hydrogen-terminated BDD surface could be obtained by treatment of oxygen-terminated BDD surfaces with hydrogen plasma or heating at high temperatures (800–1000°C) under hydrogen atmosphere. The hydrogen-terminated BDD electrodes have high stability and sensitivity for analysis of a number of biological species, and the performances for the detection of several selected biomolecules are summarized.

Ivandini et al. reported that oxalic acid could be electrochemically detected at as-deposited BDD electrodes [29]. The BDD electrodes exhibited well-defined peaks of oxalic acid oxidation, as shown in Figure 5, with a linear response range of 0.05–10 μM and a detection limit of ~0.5 nM (S/N = 3). For comparison, at a glassy carbon electrode, an ill-defined peak and a high background signal were observed. Clearly, the as-deposited BDD electrode showed higher sensitivity than the bare glassy carbon electrode for the detection of oxalic acid because of its low and stable background current. Moreover, at an oxygen-terminated BDD electrode, no peak was observed within the cycling potential from 0 to 2.2 V (versus Ag/AgCl), which could be ascribed to the repulsion between the negative electrode surface and the negatively charged molecules due to its two

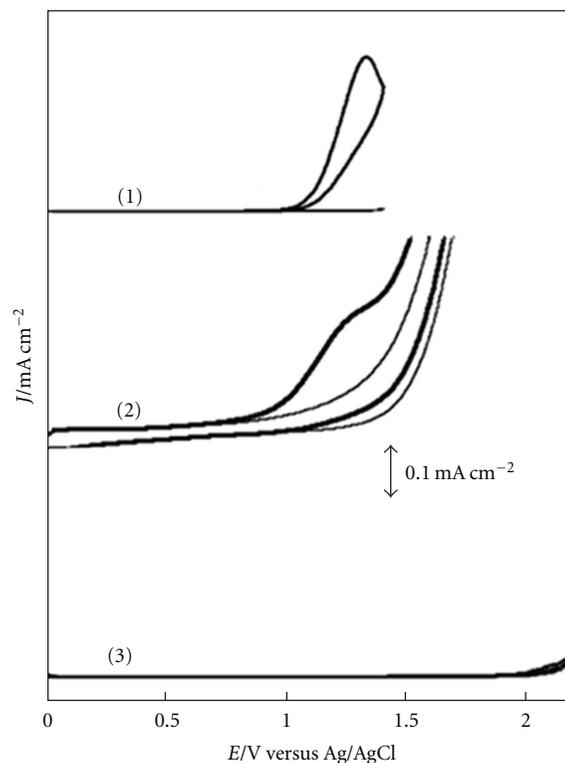


FIGURE 5: Cyclic voltammograms of 0.1 M PBS (pH 2.1) at the as-deposited (hydrogen-terminated) BDD (1), glassy carbon (2), and oxygen-terminated BDD (3) electrodes with (bold line) and without (thin line) the presence of 100 μM oxalic acid. The scan rate was 100 mV s⁻¹.

carboxyl functional groups, suggesting that surface termination contributed highly to the control of the electrochemical reaction.

L-cysteine (CySH), a sulfur-containing amino acid, plays crucial roles in biological systems, and its deficiency is associated with a number of clinical situations, for example, liver damage, skin lesions, slowed growth, and AIDS. Therefore, it is very important to investigate the electrochemical behavior and sensitive detection of CySH. Noble metal and bare carbon electrodes have been used for the study of CySH oxidation reaction, but, in this case, the detection selectivity and sensitivity was low due to the high potential. Although high electrocatalytic activity was observed at chemically modified electrodes, the activity inevitably decreased with time.

Spătaru et al. reported the studies of the electrochemical oxidation of CySH at as-deposited BDD electrodes [30]. Voltammetric and polarization studies showed that the CySH oxidation mechanism at BDD electrodes involved the dissociation of the proton from the thiol group, followed by the electrochemical oxidation of the CyS⁻ species, while, at glassy carbon electrodes, the electrochemical oxidation reaction was controlled by the desorption of the reaction products. For this reason, CySH oxidation had higher stability and sensitivity at BDD electrodes compared to glassy

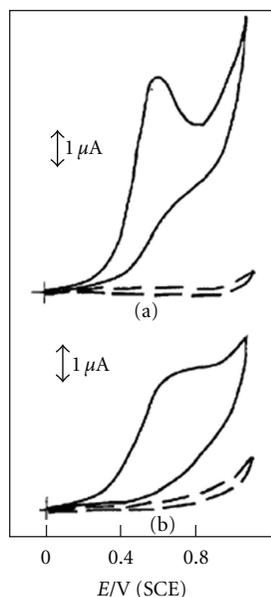


FIGURE 6: Cyclic voltammograms recorded in 0.5 M KHCO_3 containing 1 mM CySH: initial potential, 0.0 V (SCE); sweep rate, 5 mV s^{-1} . (a) BDD electrode; (b) GC electrode. (Dashed lines represent background current.)

carbon electrodes. Micromolar concentration range of 0.1–100 μM and low detection limit of 21 nM ($S/N = 3$) were obtained for CySH detection at the BDD electrodes. The deactivation of the electrode with time, which was common at the chemically modified electrodes, was also avoided due to the extreme electrochemical stability of the BDD electrode (as shown in Figure 6). That is to say, the use of BDD electrodes results in a simple and useful analytical procedure for the detection of CySH.

In addition, hydrogen-terminated BDD shows advantages for electrochemical oxidation of other biological compounds, especially negative charged molecules, such as nicotinamide adenine dinucleotide (NADH) [31, 32], biogenic amines [33], glucose [34–36], Tyr [37], Trp [38], Hb [39], and DNA [40–42] in the given buffer solutions, based on their wide potential window and low background current. In most of these studies, BDD electrode was found to outperform glassy carbon in terms of stability and sensitivity. Fundamental studies on BDD films have revealed that the lack of oxygen functional groups on the as-deposited BDD surface and the very low tendency for adsorption of most chemical species on the inert surface of diamond are mainly responsible for the superior performance of the BDD electrodes. Additionally, the oxidation reaction of the above biomolecules is very less at an oxygen-terminated BDD electrode because of the electrostatic repulsion between its carbon-oxygen dipoles and the negative charged compounds. However, at the hydrogen-terminated surface, the positive dipolar field created attracts the above biomolecules, facilitating the electrochemical reaction. Therefore, the control of surface termination is important for the electrochemical detection of some negative charged molecules by the use of BDD electrodes.

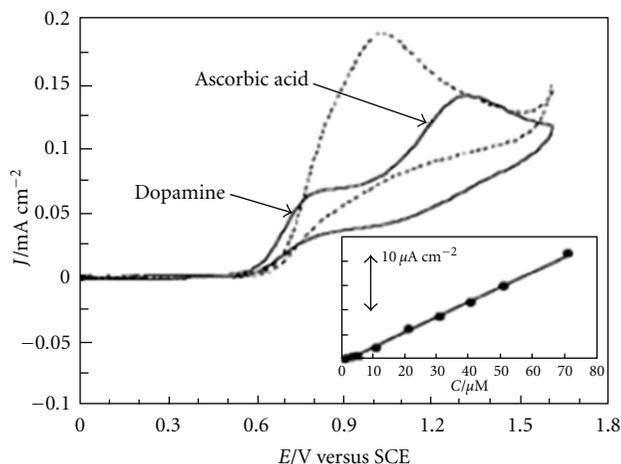


FIGURE 7: Cyclic voltammogram for a 0.1 M HClO_4 solution containing 0.1 mM DA and 1 mM AA at as-deposited and oxidized BDD electrodes. The scan rate was 100 mV s^{-1} . Inset shows a cyclic voltammogram calibration curve for DA in 0.1 M HClO_4 solution in the presence of 1 mM AA.

3.2. Electrochemical Biosensors Based on Oxygen-Terminated BDD Electrode. Dopamine (DA) is an important neurotransmitter in mammalian central nervous system. A loss of DA-containing neurons may result in serious disease such as Parkinson's disease. Recently, some nanomaterials, for example, carbon nanotubes [43], gold nanoparticles [44], and polymer thinfilm [45] modified glassy carbon electrodes, were used to carry out the simultaneous detection of DA and AA. However, there are difficulties remaining to be solved, such as complicated preparation methods and long-term stability.

Fujishima's group researched the electrochemical detection of DA in the presence of AA at BDD electrodes [46, 47]. As shown in Figure 7, at as-deposited BDD (hydrogen-terminated) electrode, the anodic peak potential ($E_{p,a}$) of DA and AA was 0.76 and 0.80 V (versus saturated calomel electrode, SCE) in 0.1 M HClO_4 , respectively. After electrochemical treatment of BDD (oxygen-terminated) electrode, the $E_{p,a}$ of DA and AA was 0.80 and 1.3 V (versus SCE), respectively. Cyclic voltammogram for a solution containing both DA and AA in 0.1 M HClO_4 at the oxygen-terminated BDD electrode exhibited two well-defined anodic peaks. Therefore, DA can be selectively determined in the presence of AA using the oxygen-terminated BDD electrode, and, as a result, a low detection limit of 50 nM ($S/N = 3$) was obtained. Possible explanation of the selective detection for DA is that the oxidized BDD surface acquires surface dipoles as a result of introducing C=O functional groups, which then electrostatically repel the oxygen-containing group on AA with strong dipoles. That is to say, the AA oxidation is impeded owing to the high potential required and the spatial locations separates from oxidized BDD surface. For the protonated DA, the interaction between the ammonium group of DA is relatively strong with both hydrogen- and oxygen-terminated BDD electrode, so that the equilibrium

distances and the electron transfer rates are not greatly different.

Popa et al. reported the selective detection of UA in the presence of AA at anodized BDD electrodes [48]. The C=O groups of BDD electrodes were expected to form a surface dipolar field, which repelled AA molecules that have oxygen-containing functional groups surrounding a central core, as noted in Section 3.1. In differential pulse voltammograms, the oxidation peak potential of AA was ~ 450 mV more positive than that of UA at oxidized BDD electrodes. Thus, the detection of UA could obtain excellent selectivity and sensitivity with a detection limit of 1.5×10^{-8} M ($S/N = 3$) in the presence of high concentrations of AA by use of chronoamperometry. Meanwhile, the oxidized BDD electrode exhibited high reproducibility and long-term stability (repeatedly used for more than 3 months), and the practical analytical utility was demonstrated in human urine and serum.

Moreover, Terashima et al. studied the amperometric detection of GSSG and GSH at anodically oxidized BDD electrodes [49]. Ivandini et al. described the simultaneous detection of purine and pyrimidine bases at BDD electrodes [50]. At anodized BDD electrode, well-defined anodic peaks were observed for the oxidation of purine and pyrimidine bases in acid medium due to its high overpotential of oxygen evolution reaction. In brief, the oxygen-terminated BDD electrodes have outstanding features in a much wider potentials window and higher surface stability from fouling compared to hydrogen-terminated BDD electrodes. Importantly, the oxygen-terminated BDD electrodes are able to achieve selective detection of certain compounds under certain conditions. The significant advantages including very ease of preparation, very high stability, high sensitivity, and good selectivity make oxygen-terminated BDD electrodes an interesting candidate for the study of the direct detection of biological molecules.

3.3. Biosensors Based on Amine-Terminated BDD Electrodes. Generally, amine-terminated BDD electrodes could be achieved by modification of several methods, such as etching a hydrogen-terminated BDD surface by NH_3 plasma, chemical modification of an oxidized BDD surface with (3-aminopropyl) triethoxysilane [51], photochemical reaction of amino molecules by free radical mechanism [52], and diazonium functionalization of 4-nitrobenzediazonium tetrafluoroborate with combined chemical and electrochemical processes [53]. Thus, a layer of amine groups introduced on the BDD surface could serve as binding sites for attachment of biomolecules.

Notsu et al. reported the immobilization of tyrosinase on a BDD electrode. Firstly, (3-aminopropyl) triethoxysilane was used to modify BDD electrode treated by electrochemical oxidation and then a tyrosinase film cross-linked with glutaraldehyde. The low limit with 10^{-6} M for bisphenol-A was achieved at the enzyme electrodes by using a flow injection system. However, the tyrosinase-modified BDD electrode retained its initial activity only for a few days in storage under dry conditions, due to weak bonding of (3-aminopropyl) triethoxysilane with BDD surface.

To improve the stability of tyrosinase-based BDD electrodes, Zhi's group studied the covalent immobilization of tyrosinase onto the amine-terminated BDD electrode [54, 55]. The amine active BDD surfaces were obtained by two methods. One was that the hydrogen-terminated BDD surface was treated with allylamine by photochemical reaction. Another was that the hydrogen-terminated BDD surface was treated with 4-nitrobenzediazonium tetrafluoroborate. Both of the two tyrosinase-modified BDD electrodes by the above methods exhibited fast response, high sensitivity, and wide linear range for the detection of phenolic compounds, as shown in Figure 8 (taking diazonium method as an example). The sensitivity of the enzyme electrode by diazonium method was also higher than those of the tyrosinase biosensors reported [56–58], which could be attributed to the high and reliable loading of enzyme by present method. The two developed enzyme electrodes could retain about 90% of its initial activity for the response of phenols after 1 month. The high stability could be ascribed to the strongly covalent bonding of tyrosinase to the BDD electrodes and the high chemical and electrochemical stability of the BDD substrates. To sum up, the amine-functionalized BDD electrodes is an interesting alternative for application in biosensing technology.

3.4. Biosensors Based on Carboxyl-Terminated BDD Electrodes. The sp^2 -bonded carbon phase on grain boundaries of nanocrystalline BDD films can provide charge carriers and high carrier mobility pathways, which may lead to better reversible properties of electrodes for redox systems [59]. Thus, BDD electrode is expected to be a more suitable candidate to provide a high activity for biosensors. Zhi's group reported the functionalization of nanocrystalline BDD films via photochemical reaction with undecylenic acid methyl ester and subsequent removal of the protection ester groups to produce a carboxyl-terminated surface [60]. Then cytochrome *c* was successfully immobilized on nanocrystalline BDD electrode by the bonding of negatively charged carboxylic groups and positively charged lysine residue of Cyt *c* (pI 10). The cytochrome *c*-modified nanocrystalline BDD electrode showed a pair of quasi-reversible redox peaks with a formal potential (E^0) of 0.061 V (versus Ag/AgCl) in 0.1 M PBS (pH 7.0) and a high electron transfer constant (k_s) of $5.2 \pm 0.6 \text{ s}^{-1}$.

Photochemical surface reaction between hydrogen-terminated BDD and 4-pentenoic acid was used to modify the BDD electrode surface, producing carboxyl-terminated surface [61]. The differential pulse voltammogram for the solution containing DA and AA at the above carboxyl-terminated surface showed well-separated oxidation peaks for DA and AA at 0.4 and 0.6 V, respectively, and the sensitivity enhanced distinctly than the oxygen-terminated BDD electrodes. The good selectivity and sensitivity were partly due to simple electrostatic effects and partly due to suppression of the polymerization of DA oxidation products by the terminal carboxyl groups.

3.5. Biosensors Based on Metal (Oxide)-Modified BDD Electrodes. Assembly of ordered metal (oxide) nanoparticles, in

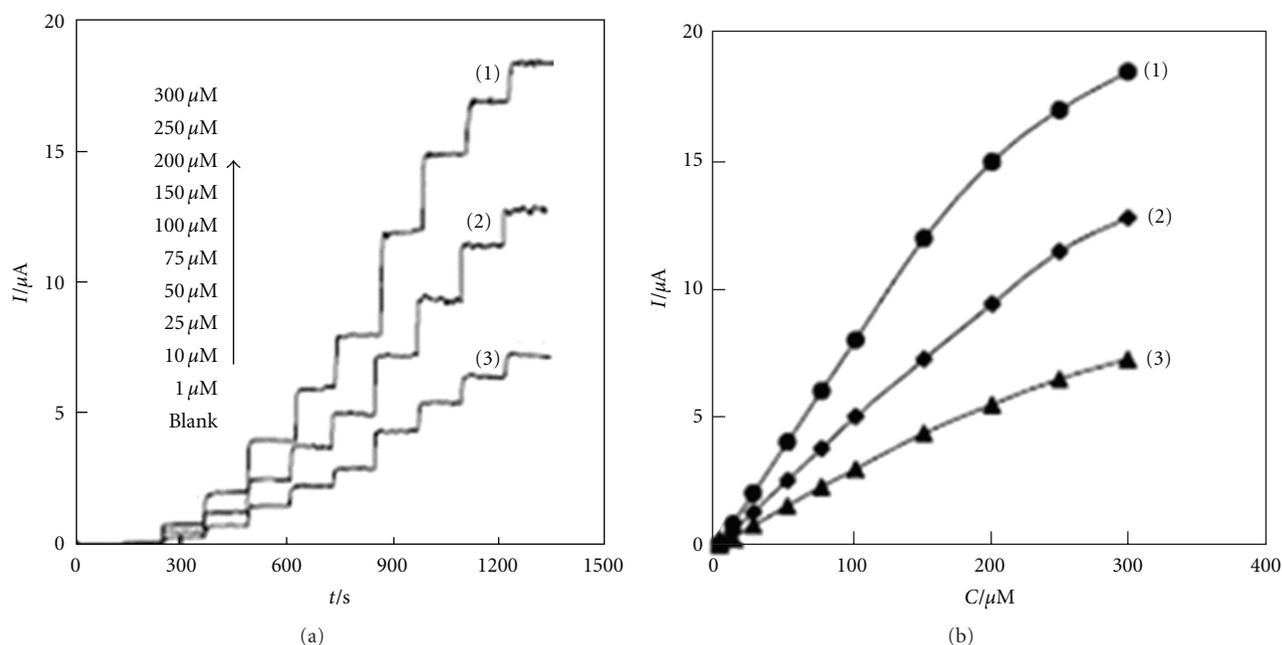


FIGURE 8: (a) Current-time recording and (b) calibration curve of the tyrosinase-modified BDD electrode to p -cresol (1), 4-chlorophenol (2), and phenol (3). Supporting electrolyte was 0.1 M PBS (pH 6.5). Applied potential was -0.15 V versus SCE.

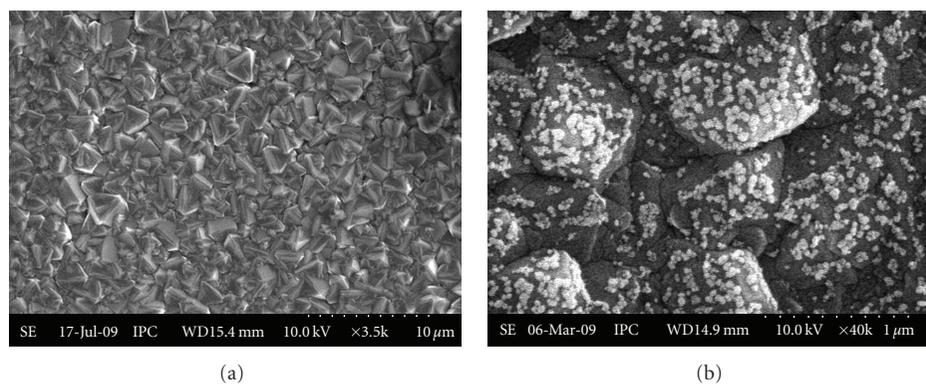


FIGURE 9: SEM images obtained from the BDD (a) and OT-Au-BDD (b) surfaces.

particular gold nanoparticles, has a wide range of applications in electronics, catalysis, and analysis. Metal (oxide) nanoparticles could be immobilized on diamond surface by vacuum vapor deposition, electrochemical deposition, sputtering, or layer-by-layer self-assembly.

Wang et al. designed an octanethiolate gold particles modified boron-doped diamond (OT-Au-BDD) electrode for CPB analysis (Figure 9) [62]. The alkane chains come from octanethiol used as an adsorbent of CPB on the surface of electrode, and the length of alkane chain was chosen in a suitable range which made the adsorbent not deteriorate the electron transfer too much. The obtained OT-Au-BDD electrode displayed a detection limit of $0.2 \mu\text{M}$ and good reproducibility in CPB analysis. Weng et al. reported that BDD electrode was modified with gold clusters by electrodeposition and the electrochemical performance of DA and AA was investigated on the Au/BDD electrode

[63]. The electrochemical oxidation of purine bases, adenine or guanine, and DNA have been investigated at a nickel nanoparticle modified boron-doped diamond electrode by Harfield et al. [64]. An oxidative response was observed at the Ni-BDDE for each analyte, particularly notable of the adenine as the oxidation overpotential was reduced to below 0.5 V versus SCE and was otherwise unobserved at the unmodified electrode. Other metal nanoparticles modified BDD electrode, such as antimony [65], bismuth [66], cobalt [67], copper [68–70], and platinum [71–73], have been widely investigated. The benefits and use of nanoparticles in electroanalysis are discussed in more detail in the extensive review by Welch and Compton [74] in 2006 that was recently updated by Campbell and Compton [75].

Terashima et al. demonstrated the electrocatalytic activity of hydrous iridium oxide (IrO_x) modified on BDD electrodes by electrodeposition [76]. Highly dispersed and stable IrO_x

nanoparticles could be obtained by the control of the deposition conditions, and the deposition of a low amount of IrO_x (ca. 2 nmol cm⁻²) on the BDD electrode exhibited an excellent analytical performance for H₂O₂ detection with a wide dynamic range (0.1–100 μM). The sensitivity for H₂O₂ was ca. 10 times higher than that of the usual Pt-bulk electrodes. Furthermore, the IrO_x modified BDD electrodes enabled H₂O₂ detection in neutral media, which was an advantage compared to sensors obtained by IrO_x deposition on other substrates.

In brief, the modification of metal (oxide) nanoparticles on the BDD electrode makes it a candidate to prepare highly active electrode for the catalytic oxidation (or reduction) of biomolecules. Especially, the immobilization of charged nanoparticles on BDD electrode could determinate special biomolecules in biological system with high selectivity and high sensitivity. The metal nanoparticle modification of BDD offers a simple yet effective approach to enhancing the electroanalytical ability of the electrode material.

4. Conclusions

In conclusion, several functional BDD electrodes, including nanostructured BDD surface electrodes, and chemically modified BDD surface electrodes, such as hydrogen-terminated, oxygen-terminated, amine-terminated, and carboxyl-terminated and metal-modified BDD films, have been used for determining various bioanalytes over the past decade or so. Because of the excellent properties of BDD substrates, these BDD-based biosensors exhibited good performances in terms of high sensitivity, selectivity, reproducibility, and long-term stability. That is to say, BDD electrodes are interesting candidates for the construction of electrochemical biosensors or the direct electrochemical detection of biomolecules.

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