Polish J. Chem., **78**, 1319–1325 (2004)

Modification of Boron-Doped Diamond Thin Film Surface by Covalent Attachment of Redox Active Molecules[*]

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(Received March 11th, 2004; revised manuscript April 26th, 2004)

This paper reports on the formation of adipoyl chloride adlayer covalently bound through an ester-like bond to the surface of boron-doped diamond electrode. The exposed functional groups of this monolayer can participate in subsequent surface reaction with aminomethylpyrene electroactive fluorophore molecules *via* the carbodiimide chemistry. Since pyrene derivatives are frequently used as polarity-sensitive optical probes, the ability to covalently bind such probes to variety of surface will broaden the field of relaxation dynamics studies of these molecules.

Key words: boron-doped diamond electrode, surface functionalization, covalent attachment

The fabrication of functional electrode surface is attractive from both the scientific and technological points of view. Therefore, boron-doped diamond thin films have emerged as important electrode materials because of their wide potential window, low background current improving the signal-to-noise ratio (approximately an order of magnitude comparing to glassy carbon), as well as mechanical and chemical robustness, especially under extreme conditions at very positive potential region. Moreover, boron-doped diamond (BDD) films retain favourable optical properties of diamond [1–4]. The high stability of BDD films is due to their relative chemical inertness. While this property is beneficial from the point of view of electrode stability, it may limit the use of such material where the surface modification imparting electrode selectivity is required.

The electrochemical modification of BDD films has been reported before, yet it was limited to diazonium salts, alkenes and substituted aromatic groups [5–9]. Our recent works have shown that simple displacement reaction can result in a covalent adlayer growth on a variety of surfaces ranging from silica, oxidized silicon, indium-doped tin oxide (ITO) and electrochemically generated gold oxide surfaces [10,11]. Lately, the usefulness of such chemistry was demonstrated also for the case of modification of boron-doped diamond surface [12]. The common motif in all these

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

cases is the reaction of surface functional hydroxyl groups with an acid chloride. The resulting interface is stable and resistant to organic solvents and elongated use as measured electrochemically and spectroscopically.

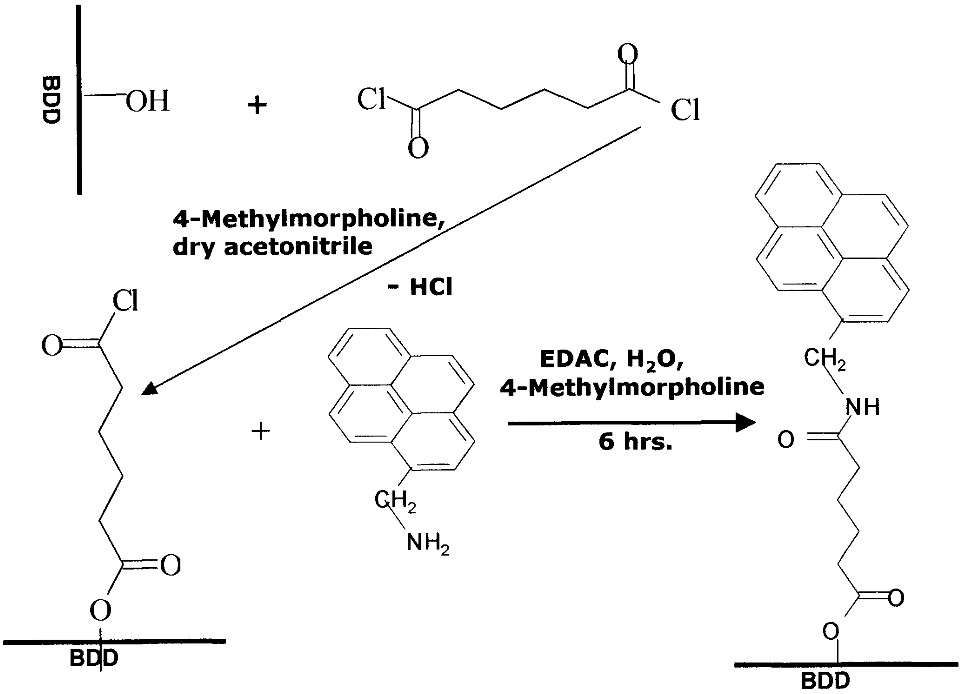
This paper reports on the covalent attachment of aminomethylpyrene electroactive fluorophore molecules *via* carbodiimide chemistry to BDD surface that was first modified with covalently bound adipoyl chloride adlayer. This procedure yielded almost ten times higher surface coverage with fluorophore molecules as compared to reported in the literature [12]. Since pyrene derivatives are frequently used as polarity-sensitive optical probes, the ability to covalently bind such probes to variety of surfaces will broaden the field of relaxation dynamics studies of these molecules.

EXPERIMENTAL

Chemicals: Boron-doped diamond thin films on quartz slides were generously provided by Professor G.M. Swain, Chemistry Department, Michigan State University, USA. All chemicals were of the highest quality commercially available: 1-aminomethylpyrene hydrochloride (Aldrich, 97%), adipoyl chloride (Aldrich, 98%), 4-methylmorpholine (Aldrich, 99%), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC, Sigma) acetonitrile (Aldrich, anhydrous, 99.93%), perchloric acid (Merck 70%). Aqueous solutions were prepared from water of high purity.

BDD surface modification: Typically, the surface of diamond thin film is terminated by hydrogen that renders it hydrophobic. By exposing the BDD to strong oxidizing agents, the formation of surface hydroxyl and carbonyl groups with submonolayer coverage has been reported [13,14]. Thus, the microcrystalline BDD film was treated with piranha solution in 40°C over 10 minutes, obtaining a hydrophilic surface. Next, this surface was reacted with adipoyl chloride by immersing the BDD-covered quartz slides in dry acetonitrile containing adipoyl chloride, using 4-methylmorpholine as a Lewis base (solution content: 20:1:1, v/v/v). The reaction was kept under nitrogen for *ca.* 12 h at room temperature. The substrates were removed from the reaction vessel, rinsed with the abundance of acetonitrile, methyl alcohol and dried under the stream of nitrogen. Next, the resulting terminal acid functionalities were hydrolysed to carboxyl groups by immersing the substrates in 20 ml ethanol/water solution (1:1, v/v). To this mixture 5 mL of 0.5 mM EDAC in ethanol was added in order to activate the carboxyl groups, followed by 5 mL of 0.5 mM aminomethylpyrene in ethanol (aminomethylpyrene hydrochloride was converted into free base *in situ* by the addition of equimolar amount of 4-methylmorpholine). After completion of the reaction (typically *ca*. 6 hrs under nitrogen at 25°C), the substrates were removed, rinsed with abundance of water, then ethanol, dried and used in electrochemical measurements. The schematic drawing of procedure described above is shown in Scheme 1.

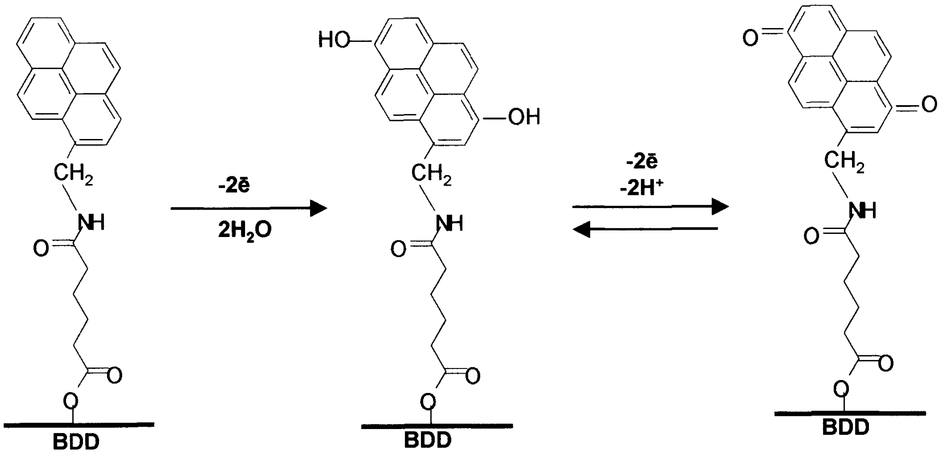
Electrochemistry: Electrochemical measurements were conducted with a PC-controlled KSP DPTG-360 potentiostat/galvanostat (KSP Instruments, Poland), using a small-volume, three-electrode cell with a Pt wire as the counter electrode. All potentials are quoted *versus* a Ag/AgCl ≠ 1 M KCl_{aq} reference electrode. Electrochemical measurements on boron-doped diamond thin film electrode (0.22 cm^2 working area, determined with use of a standard ferric/ferrous hexacyanide redox couple, as reported elsewhere [15]) were carried out in aqueous 0.1 M $HClO_4$ solution.



Scheme 1. Schematic drawing of BDD surface modification by covalent adipoyl chloride attachment to the surface with subsequent bonding of aminomethylpyrene.

RESULTS AND DISCUSSION

Fig. 1a, b, presents a series of voltammetric scans for aminomethylpyrene immobilized on boron-doped diamond thin film surface recorded in 0.1 M $HClO_{4\,aq}$. In the first scan (Fig.1a), when the anodic potential above *ca.* 1.1 V is applied to the electrode, one can observe an irreversible "hump" with maximum at 1.05 V. With the reverse scan, as well as in subsequent scans, a pair of new redox peaks around 0.32 V appear in voltammograms. Consecutive scanning results in the disappearance of irreversible "hump" while the new pair increases its magnitude and seem to be the final products of pyrene oxidation. These changes are indicated by arrows in Fig. 1b. Here it is anticipated that the irreversible "hump" at 0.96 V can be assigned to oxidation of pyrene molecules and formation of radical cations [16,17]. As the radical cations are highly reactive, one does not observe a reduction peak, as the formed species immediately follow further chemical transformations including a variety of reaction paths including introduction of hydroxy and carbonyl groups to the ring system, dimerization, *etc.* [17–20]. Based on the thorough and complex analysis of electrochemical reactions of surface-bound pyrene molecules on gold and ITO surfaces reported in literature [16], where similar voltammetric signals around 0.33 V were reported for 1,6-pyrenedione reducing to 1,6-dihydroxypyrene, the new pair of redox peaks centered at 0.30 is assigned to 1,6-dihydroxy derivative of pyrene formed on BDD thin film by electrochemically generated radical cations in aqueous media, Scheme 2.



Scheme 2. Scheme of redox reaction of surface-confined pyrene derivatives assigned to CV curve shown in Fig. 1b.

Fig. 2 shows the final voltammogram where only one set of peaks attributed to 1,6-dihydroxy derivative of surface-confined aminomethylpyrene is visible. In order to verify the surface behaviour of observed voltammogram the anodic peak height *versus* scan rate was plotted in 0.1 M $HClO_4$ aqueous solution (Fig. 2, inset). Linearity of this graph confirmed its surface nature.

Integration of the amidopyrene oxidation surface charge yields a surface coverage of 3.3×10^{-11} mol cm^{-2} (assuming 2-electron process [16,20]), less than expected for coverage observed for gold [16] and *ca*. 20 times times smaller than the density reported for alkanethiol monolayers self-assembled on gold (7.7×10^{-10} mol cm^{-2} [24]). Nevertheless, taking into account the inertness of BDD surface and much lower density of similar redox active groups achieved in literature (4.25×10^{-12} mol cm^{-2}), the modification procedure reported here results in *ca.*10 times higher yield. The quality of the electroactive adlayer can be assessed from CV peak symmetry, its width and peak-to-peak separation at low scan rates. The observed peak separation never decreases to zero, but remains at a value of *ca.* 60 mV for scan rates below 0.1 V/s, indicating interactions between redox centers. The peak widths of 120 to 150 mV for the slowest scan rates indicate a distribution of distances of the redox centers from the

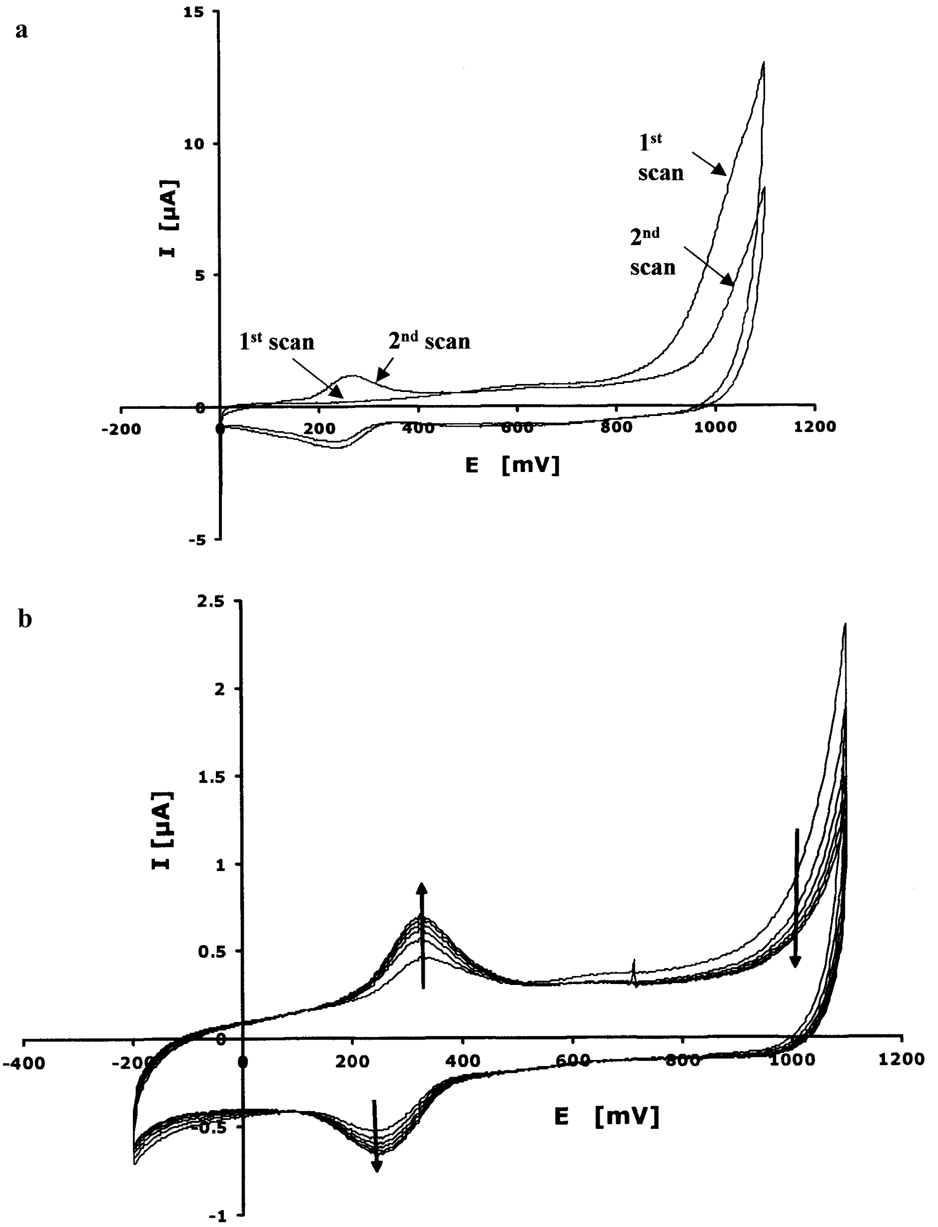


Figure 1. Consecutive voltammetric scans for aminomethylpyrene immobilized on boron-doped diamond thin film surface recorded in 0.1 M $HClO_{4\,aq}$. Scan rate 50 mV/s.

electrochemically active surface and/or strong interactions between them [21–23]. Even though the low surface coverage suggests rather only the former, our previous works on the time-domain fluorescence response of tethered pyrene derivatives on BDD suggest large orientational distribution of the substrate surface in addition to the presence of the aggregated form of the surface-bound pyrene. Further studies are being carried out to get a deeper insight into the organization of the adlayers tethered to the BDD surface.

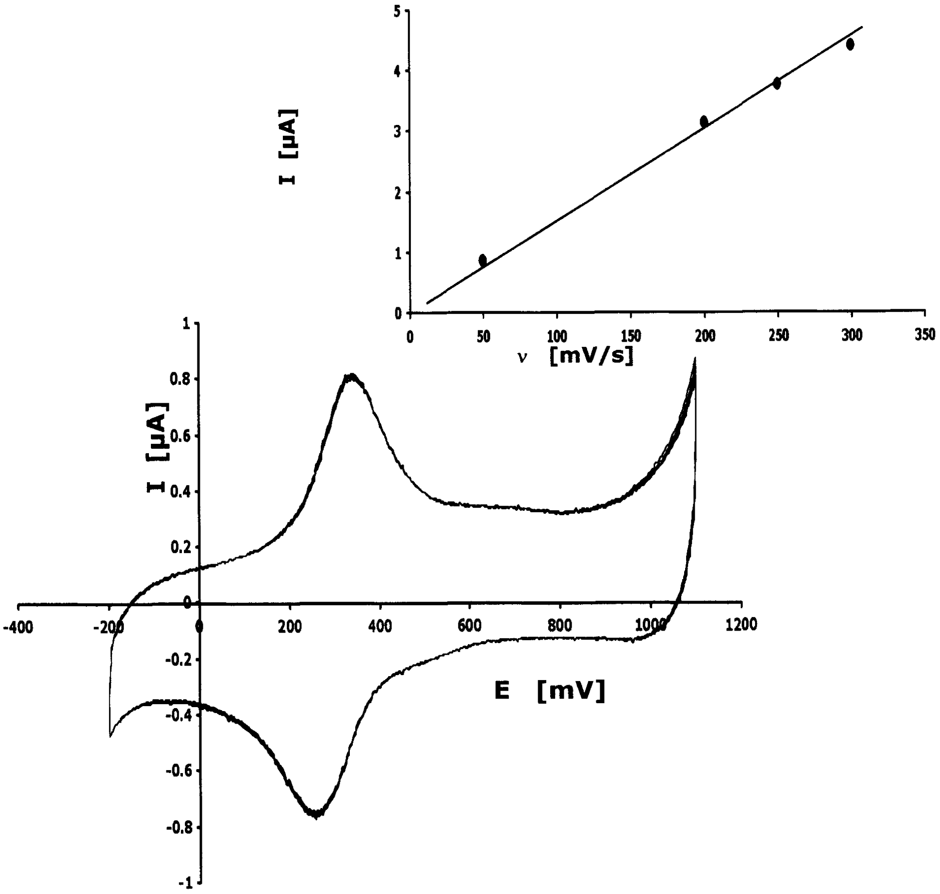


Figure 2. Cyclic voltammogram of aminomethylpyrene-modified BDD surface in 0.1 M $HClO_{4\,aq}$, 50 mV/s scan rate. Inset: Dependence of peak current on scan rate.

CONCLUSIONS

Boron-doped diamond thin film electrode surface was modified by a covalent attachment of electroactive organic molecules of aminomethylpyrene. The density or redox centers was evaluated by means of cyclic voltammetry, based on its known electrochemistry. The obtained value of 3.3×10^{-11} mol cm^{-2} is relatively high, taking into account the inertness of BDD surface. The reported procedure opens up new capabilities to control the reaction mechanisms and kinetics on boron-doped diamond thin film electrodes, through modifications of surface chemistry. Further work is being carried out concerning the surface organization of the adlayer-forming molecules and their density.

Acknowledgment

The author is grateful to Professor Greg M. Swain, Chemistry Department, Michigan State University, USA, for his generous gift of boron-doped diamond thin films made in his group by the low-pressure chemical vapour deposition growth on quartz slides.

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