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The Effect of pH on Electro-oxidation of Phenolic Compounds at Boron-Doped Nanocrystalline Diamond Films (BDND)

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The surface properties of boron-doped nanocrystalline diamond (BDND) films were investigated in regard to their electrochemical response to phenol, 4-chlorophenol and 4-nitrophenol. The films were produced using Hot Filament CVD technique on Si substrate with a gas mixture of $CH_4/H_2/Ar$. The morphology and quality of the BDND electrode were characterized by scanning electron microscopy and by Raman scattering spectroscopy. The BDND surface pre-treatment was carried out to evaluate the phenolic compounds detection efficiency induced by anodic polarization (AP) followed by cathodic polarization (CP) in 1 mmol L^{-1} of these compounds in different pH range from 1 to 13.5. The use of cyclic and linear voltammetry with the BDND electrodes for the detection of these phenolics compounds is described.

Introduction

Nowadays public concern and legislation are demanding better environmental control. Moreover, the increase in the number of analytes requires more suitable analytical methods to monitor them. Indeed, conventional methods reach the highest accuracy with low detection limits, but they are expensive, time-consuming and require the use of highly trained personnel. Nonetheless, the use of electroanalytical methods for controlling a variety of organic and inorganic substances has made it possible to reach detection limits compatible with environmental regulations. In this context, the sensors can also meet the need for their continuous use in real-time to replace the intermittent analytical techniques used in industrial processes.

The aromatic compounds, and particularly the phenolics, have high toxicity and low water solubility and are released in the wastewaters from a considerable number of industries. The phenol is fatal if ingested, inhaled and absorbed by the skin and may cause severe burns and affect the central nervous system, the liver and the kidneys. In Brazil, legal restrictions promulgated by the government define a limit value of 0.5 mg L^{-1} for all phenol compounds from industrial effluents. So, we focus our work on these analytes using boron-doped nanocrystalline diamond (BDND) as nanosensors.

However, when the subject is nanoscience and nanotechnology, it is necessary to be careful because the properties related to the particle reduction may be more important than those related to their sizes. This behavior, which is not displayed by the bulk matter, is associated with the fact that some very small structures usually have new properties. As a result of the size reduction, new effects appear and play an important role, for example, the change in the surface/volume ratio. In this sense, if the surface/volume ratio increases, the surface phenomena will predominate over the chemical and physical bulk properties [1]. Riu et al. [1] have discussed the main concepts behind the development of nanosensors and the most relevant applications in the field of environmental analysis. They showed that the important characteristics and the quality parameters of the nanosensors can be improved over the case of classically modeled systems merely by their size reduction. For example, the advantages of using nanosensors are the following: (a) the sensitivity can increase because of better conduction properties; (b) the limits of detection can be lower; (c) small quantities of samples can be analyzed; (d) a direct detection is possible without using labels; (e) some reagents can be eliminated.

Over the past years, the topic of interest in the scientific community has been the nanocrystalline diamond (NCD). The NCD may be produced with different crystalline structures and grain sizes depending on the growth chemistries, such as argon-rich and hydrogen-poor gas phase [2-4]. And, doped NCD films can be grown by adding nitrogen or boron to the growth mixture in order to get the n-type or p-type semiconductor materials, respectively, for electronic and electrochemical applications [2]. Boron is the most successful and widely used acceptor in diamond. The success of efficient diamond doping is largely dependent on the structural conformation of the dopant and the type of bonding surrounding the carbon atoms.

Considering the electrochemical characteristics of sensors based on BDND, several studies have reported promising results for these electrodes, such as a fast response, a low detection limit, a high stability and an excellent response accuracy [5-7]. The sensors have been classified according to multiple criteria (1). The most common way of grouping sensors take the following topics into consideration: (a) the transducing mechanism (electrical, optical, mass, etc.); (b) the recognition principle (enzymatic, DNA, molecular recognition, etc.); (c) the applications (environmental, food, medical diagnosis, etc.) [1].

In this context, this work is an extension of our previous efforts where the detection of phenol was obtained using BDND electrodes with different pre-treatments from the SWV technique [8]. Therefore, the goal of this work is to analyze the influence of pH on electro-oxidation process of phenol, 4-chlorophenol, 4-nitrophenol.

Experimental

The diamond films depositions were performed with the HFCVD technique using the following growth parameters: temperature of 900 K, pressure of 6.7 kPa, 6-hour deposition time, and gas mixture of $CH_4/H_2/Ar$ with flow of 1/19/80 sccm. Five filaments of tungsten were used and their temperature during the experiment was around 2300 K. All the films were grown on polished silicon [100] 1x1 cm^2 samples. The substrates were prepared by ultrasonic hexane bath with 0.25 μm diamond powder for 60 min. The boron doping was performed by the addition of B_2O_3 to the methanol in the bubbler. When B_2O_3 is dissolved in CH_3OH, trimethylborate $(CH_3O)_3B$ is produced, which is probably the substance containing boron that is added to the gas mixture during the growth process. A solution with the concentration of B_2O_3 dissolved in CH_3OH of 30,000 ppm of boron atoms in relation to carbon atoms of the methanol (B/C ratios) was prepared. The volume of methanol was fixed at 200 mL. This boron doping level corresponds to the acceptor density value of 10^{20} B.cm^{-3} evaluated by Mott-Schottky plot analysis (not shown). The solution was placed in a bubbler at a constant pressure and temperature, and the H_2 gas was used as a carrier with a constant flow of 30 sccm.

The morphology and quality of the films were evaluated by scanning electron microscopy (SEM) using a JEOL JSM-5310 model and by micro-Raman scattering spectroscopy (Renishaw microscope system 2000) using the 514.5 nm line of an argon ion laser taking the spectra covering the range from 300 to 3500 cm^{-1}. Electrochemical measurements were carried out using Autolab PGSTAT 302 equipment in a three-electrode compartment cell with 50 cm^3 of capacity. The BDND films were used as working electrode and their geometric area in contact with the electrolyte was 0.10 cm^2. The platinum coil and Ag/AgCl electrodes were used as counter and reference electrodes, respectively. The sweep rate of 50 mV s^{-1} and the electrolyte supports of 0.5 mol L^{-1} H_2SO_4 and NaOH at different pH (1.0, 3.0, 7.0, 9.0, 13.5) were used. The qualitative detection of phenol, 4-chlorophenol, 4-nitrophenol were carried out using linear voltammetry (LV) and cyclic voltammetry (CV) in a concentration of 1.0 mmol L^{-1}. Before each measurement the solution was stirred with N_2 (99.99%) for 10 min, and after each subsequent measurement the BDND surfaces were treated by anodic polarization (2.8 V *vs.* Ag/AgCl) for 10 s followed by cathodic polarization (-2.8 V *vs.* Ag/AgCl) for 10 s. This procedure was necessary to restore the initial electrode activity [8]. All experiments were conducted at 22 ± 2°C.

Results and Discussions

The SEM image of the BDND film and its respective Raman spectrum are shown in Figures 1 (a,b). According to the SEM images, the surface analysis showed a film with a uniform morphology and a flat surface composed of clusters of small particles with different sizes. This film has a lot of sp^2 carbon present in the grain boundaries that was confirmed by Raman spectrum analysis.

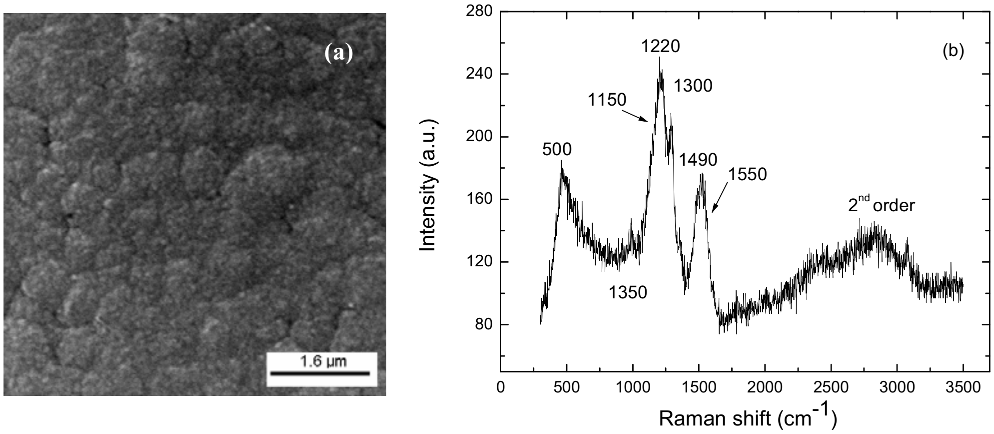

Figure 1: (a) SEM topographic image and (b) Raman spectrum of BDND electrode.

Eight features were identified in the Raman spectra of the films shown in Figure 1(b). The diamond peak was visible and shifted to a lower wavenumber (1300 cm^{-1}). This shift is related to impurities formed in heavily doped films showing a metal-like conductivity [9]. The D (1350 cm^{-1}) and G (1550 cm^{-1}) are related to high part of sp^2-bonded carbon in these films. This behavior was confirmed by the high intensity of its second order Raman spectra around 2800 cm^{-1}. The shoulders at 1150 cm^{-1} and 1490 cm^{-1} are related to transpolyacetylene (TPA) segments at the grain boundaries of the NCD surface [10]. The broad bands around 500 and 1220 cm^{-1}, which are present in the film are still subject of an intense debate. However, the two band positions agree with the two maxima of the phonon density of states (PDOS) of diamond [11]. They could therefore be connected with a relaxation of the wavevector selection rules. If so, they may well be associated with the actual boron incorporation in the lattice, rather than in the number of holes of the film bulk [12].

The cyclic voltammograms of electro-oxidation of phenolic compounds in both acid and alkaline medium are shown in Figures 2(a,b), respectively. The BDND electrode presented a well-defined current profile for all the phenol compounds. The oxidation peak potential of 4-chlorophenol, phenol e 4-nitrophenol were 1.16, 1.22 and 1.52 V *vs.* Ag/AgCl at pH=1.0 and; 0.56, 0.57 and -0.08 V *vs.* Ag/AgCl at pH= 13.5. These preliminary results showed that the electro-oxidation of phenolic compounds is possible for BDND electrodes, regardless of the medium used; furthermore, the values of the oxidation peak potential of phenolic compounds in the alcaline medium are smaller than in the acid medium. Additionally, the current values of the oxidation peaks of 4-chlorophenol and phenol are higher in the alcaline than in the acid solutions.

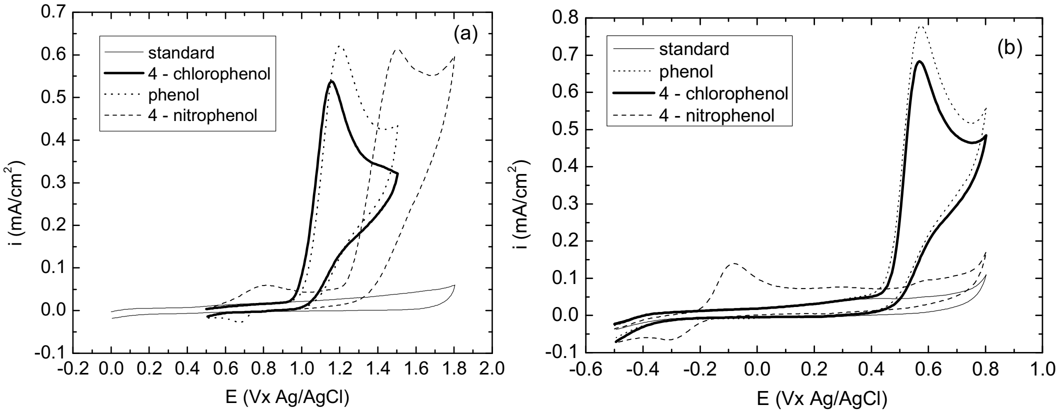

Figure 2: CV i-E curves of 1 mmol L^{-1} of 4-chlorophenol, 4-nitrophenol and phenol in 0.5 mol L^{-1} (a) pH=1.0 and (b) pH=13.5 for BDND electrode. (ν = 50 mV.s^{-1}).

Figure 3 shows the plots of the anodic peak current and the peak potential versus the square root of the scan rate in H_2SO_4 and NaOH using the BDND electrode. The anodic peak potential, as well as the corresponding peak currents for three compounds, changed as a function of the scan rate in both media. An increase in scan rate shifted the anodic peaks to more positive potentials. Besides, the anodic peak currents varied linearly but not proportionaly with the square root of the scan rate indicating a quasi-reversible behavior of this electrode. For quasi-reversible systems the current is controlled by both the charge transfer and mass transport. Thus, others criteria should be tested to confirm the quasi-reversibility of the process. For that reason, these results justify further investigations using different values of pH for future applications of this BDND electrode as nanosensors.

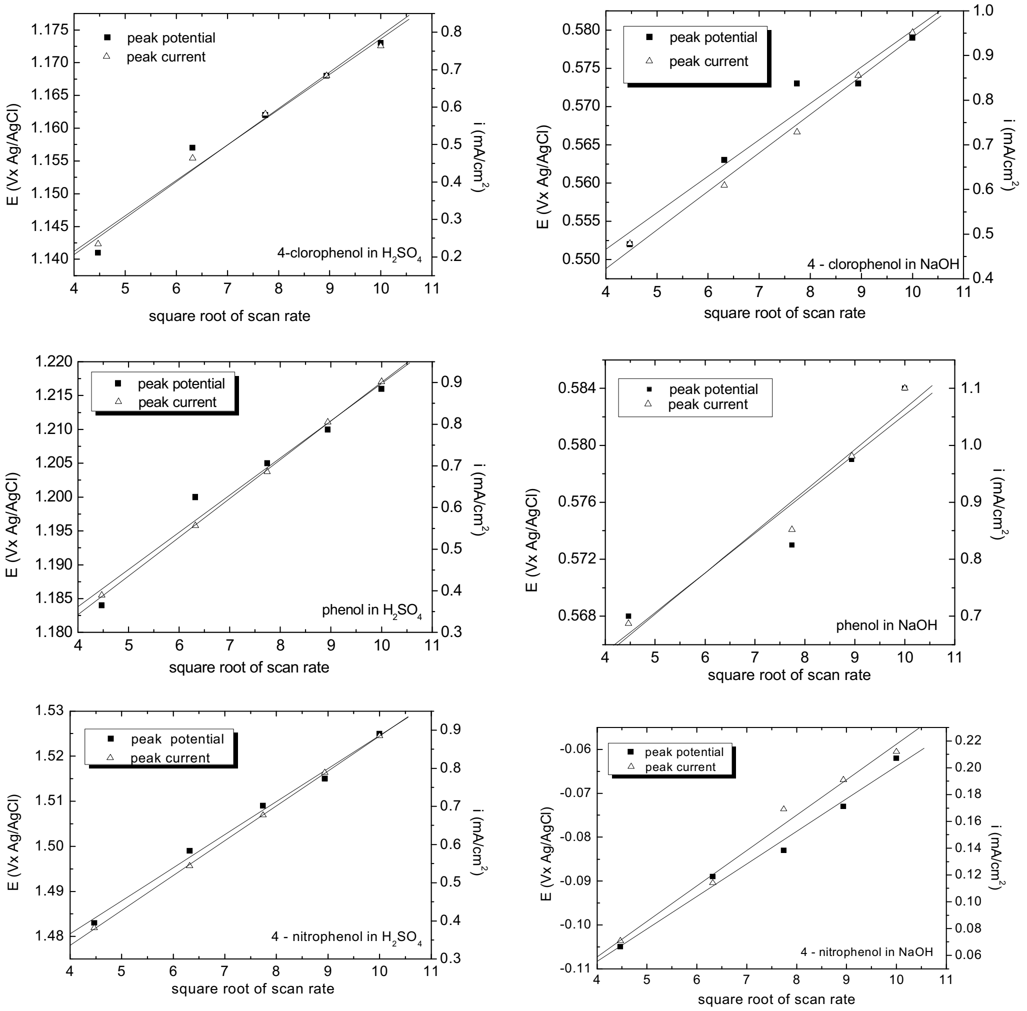

Figure 3: Plots of the anodic peak current and peak potential versus square root of the scan rate in H_2SO_4 and NaOH using the BDND electrode.

Thus, for a better understanding of the electrochemical behavior of DNDB with phenolic compounds, linear voltammograms at different pH 1.0, 3.0, 7.0, 9.0 and 13.5 were performed. The oxidation peak potential for all compounds was strongly pH-dependent as shown in Figure 4 (a-c). The peak potential of 4-chlorophenol, phenol and 4-nitrophenol were approximately the same in both pH= 1.0 and 3.0 of 1.16, 1.22 and 1.52 V *vs.* Ag/AgCl. As the value of pH increased (alkaline medium), the oxidation potential shifted to lower values. At pH = 13.5, the potential values are 0.58, 0.59 and -0.06 for the 4-chlorophenol, phenol and 4-nitrophenol. This result reflects an easier oxidation of the hydroxyl group in more alkaline medium. On the other hand, the current density *vs.* pH plot (Figure 4) revealed that the oxidation peak current has maximum values for pH 1.0 and 13.5 to 4-chlorophenol and phenol; and, for pH 1.0 to 4-nitrophenol. For this reason, the analysis involving the electrochemical detection of phenolic compounds using the BDND electrode should be carried out at pH 1.0.

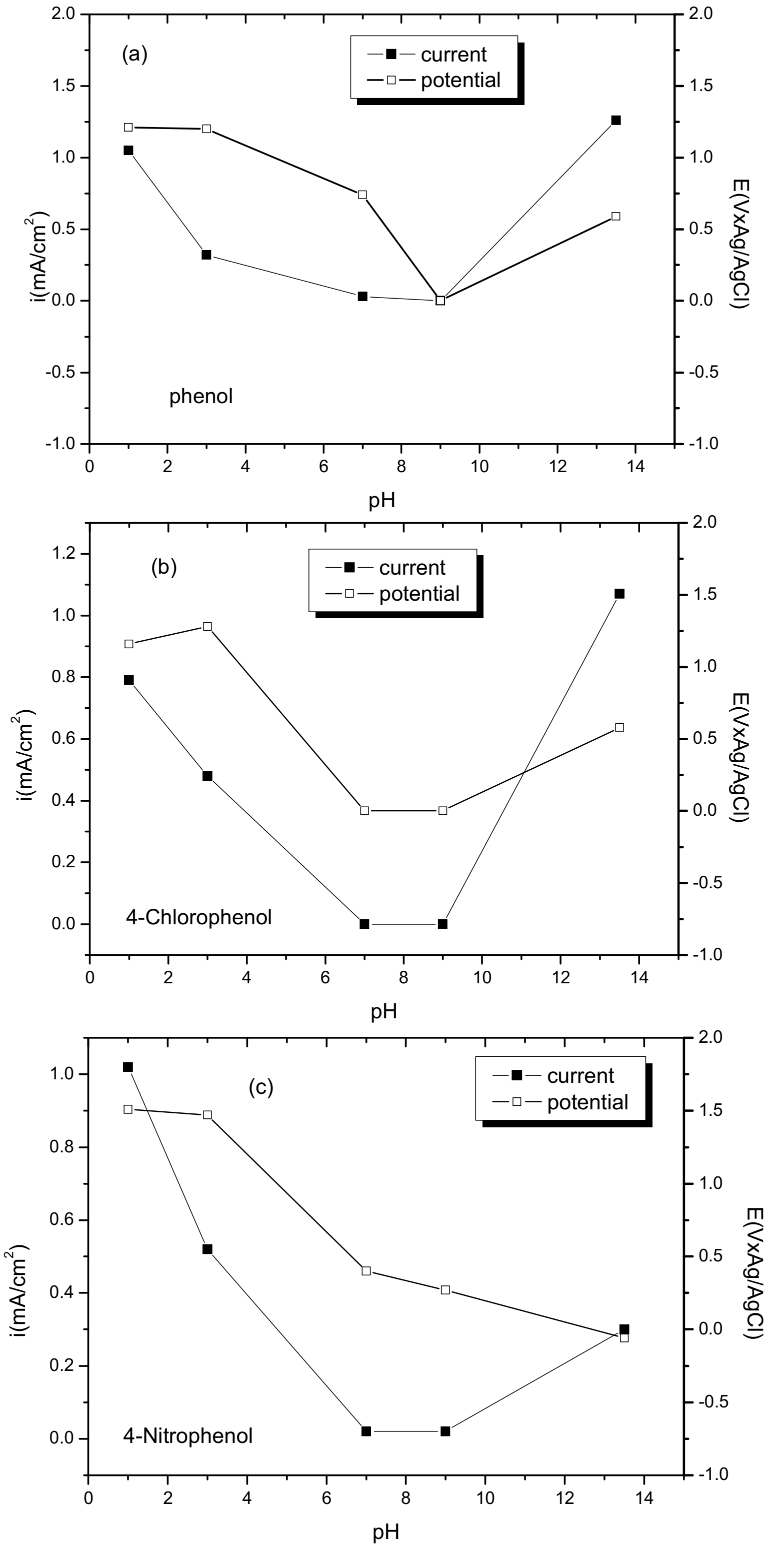

Figure 4: Influence of the pH on peak potential (□) and peak current (■) obtained from linear voltammetry i-E curves of 1 mmol L^{-1} of 4-chlorophenol, 4-nitrophenol and phenol.

Conclusions

The morphological analysis of the film surface showed a homogeneous film with the presence of small clusters of nanocrystalline grains. Its Raman spectrum confirmed the presence of large amounts of sp^2 carbon present in the grain boundaries.

The electrochemical measurements performed showed that the BDND electrode has a quasi-reversible behavior and the electro-oxidation of phenolic compounds using these electrodes is possible. Furthermore, its use in the detection of phenolic compounds showed the best results at pH=1.0 based on the plot for the current density *vs.* pH. Moreover, further research using different concentrations of phenolic compounds at pH 1.0 should be carried out in order to strengthen the use of these electrodes as nanosensors.

Acknowledgments

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References

1. J. Riu, A. Maroto and F.X. Rius, *Talanta*, **69**, 288 (2006).
2. J.E. Butler and A.V. Sumant, *Chem. Vap. Depos.,* **14**, 145 (2008).
3. O.A. Williams, M. Daenen, J. D'Haen, K. Haenen, J. Maes, V.V. Moshchalkov, M. Nesládek and D.M. Gruen, *Diam. Relat. Mater.*, **15**, 654 (2006).
4. S. Wang, V.M. Swope, J.E. Butler, T. Feygelson and G.M. Swain, *Diam. Relat. Mater.,* **18**, 669 (2009).
5. Y. Zhou, J. Zhi, Y. Zou, W. Zhang and S.-T. Lee, *Anal. Chem*., **80**, 4141 (2008).
6. J. Barek, K. Jandová, K. Peckov and J. Zima, *Talanta*, **74**, 421 (2007).
7. A.F. Azevedo, N.A. Braga, F.A. Souza, J.T. Matsushima, M.R. Baldan and N.G. Ferreira, *Diam. Relat. Mater*., **19**, 462 (2010).
8. A.F. Azevedo, F.A. Souza, J.T. Matsushima, M.R. Baldan and N.G. Ferreira, *J. Electroanal. Chem.,* **658**, 38 (2011).
9. C. Lévy-Clément, N.A. Ndao, A. Katty, M. Bernard, A. Deneuville, C. Comninellis and A. Fujishima, *Diamond Relat. Mater*., **12,** 606 (2003).
10. A.C. Ferrari, J. Robertson, *Philos. Trans. Roy. Soc. Lond. A*, **362**, 2477 (2004).
11. H. Li, T. Zhang, L. Li, X. Lü, B. Li, Z. Jin and G. Zou, *J. Cryst. Growth*, **312**, 1986 (2010).
12. M. Bernard, A. Deneuville and P. Muret, *Diamond Relat. Mater.*, **13**, 282 (2004).