Influence of the sp^2 content on boron doped diamond electrodes applied in the textile dye electrooxidation

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Several studies have been conducted to develop new technologies for the waste-water treatment, since organic contaminants have become a global problem mainly due to the population growth. The electrochemical methods have shown high efficiency in the waste-water treatment because of its versatility, low cost, and high efficiency by using the electron as the main reagent. This work presents the production and the characterization of Boron-doped diamond (BDD) films deposited on Titanium (Ti) substrate (BDD/Ti) with different sp^2 contents. The electrooxidation of the dye Reactive Orange 16 (RO16) is studied systematically considering sp^2 bonds influence. Diamond films were grown on titanium substrate of 2.5 x 2.5 cm by hot filament chemical vapor deposition technique at CH_4 additions of 1, 2, 6 and 10 sccm diluted in H_2 for a total flow rate of 200 sccm. The boron source was obtained from a constant flow of 40 sccm for an additional H_2 line passing through a bubbler containing the B_2O_3 dissolved in methanol with B/C ratio 15000 ppm. This doping level corresponds to 10^{20} cm^{-3} evaluated by Mott Schottky measurements. Electrochemical measurements were made using a platinum mesh as a counter electrode and $Ag/AgCl/KCl_{(sat)}$ as the reference electrode. The electrooxidation experiments were performed at current density of 50 mA cm^{-2} using 150 mg L^{-1} of the RO16 azo-dye and K_2SO_4 0,1 mol L^{-1} (pH= 10), in a total treatment time of 90 min. The RO16 azo-dye electrochemical degradation was monitored by: (1) UVVisible (UV/VIS) Espectrophotometry (Varian Cary 50 Scan Espectrophotometer 300 a 600 nm); (2) RO16 azo-dye concentration (HPLC, Shimadzu, modelo 20 A, with UV/VIS SPD-20 detector, C18 (250 x 4,6 mm) Shimadzu ShimPack CLC-ODS® collum, ammonium acetate/methanol (70:30), 0,8 mL min^{-1} flux and UV/VIS detector at λ= 254 nm; and (3) Total Carbon Organic (TOC, Shimadzu TOC-VCPN analyzer). The top view SEM images of one sample set doped with B/C ratio of 15000 ppm show continuous and homogeneous films covering the entire substrates. Considering the challenge to grow diamond on Ti, the films are very adherent, without cracks or delaminations (Figure 1).

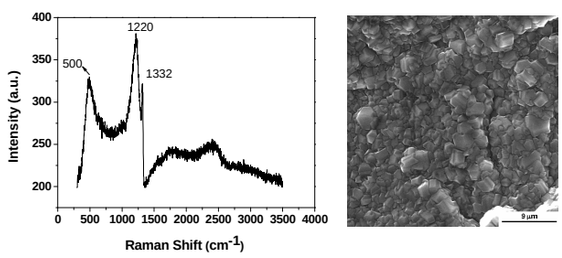

Figure 1: Spectra Raman and scanning electron micrographs of diamond films grown on titanium substrate with 15000 ppm.

The BDD morphology is associated to the microcrystalline grains randomly oriented with dominant (111) direction. As expected, the microcrystalline grain agglomerates of the diamond films increased with the CH_4 addition in the gaseous mixture. This transition is clear from 1 to 6 sccm of CH_4. Visible Raman spectroscopy confirmed the good quality of the BDD film by the presence of the narrow band at 1332 cm^{-1} which corresponds to the vibration of a diamond first-class phonon and is the diamond signature [1]. There is the appearance of the two bands located at 500 cm^{-1} and 1220 cm^{-1} attributed to B-B vibrations and B-C vibrations, respectively (Figure 1). X-ray diffraction showed diamond diffraction planes, assuring the material crystallinity. Besides, it was identified carbides (TiC) and hydrides (TiH) patterns in the film/substrate interface. The electrochemical oxidation of 0.35 L of a RO16 solution was held in a home-made cylindrical polypropylene cell. An anode in disc form (BDD/Ti) with 2.3 cm in diameter exposed area was positioned at the base of the cell. The cell temperature was kept constant at 25 ºC and the system was kept under stirring. Under these experimental conditions, the results showed that the BDD/Ti electrode was efficient in the degradation of RO16. The electrode with a lower percentage of CH_4 showed the best efficiency with respect to the reduction aromaticity and in the fracture azo group of the dye, analyzed from the UV/VIS (Figure 2), the TOC measurements as well as from the HPLC data. The results confirm the strong influence of sp^2 content on diamond films when applied in organic oxidation process.

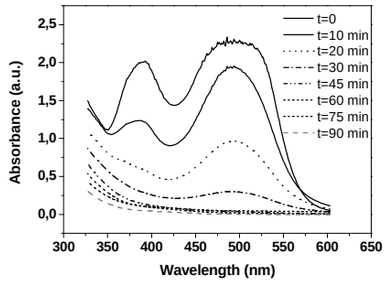

Figure 2: UV / VIS spectral changes of the RO16 azo dye in aqueous solutions as a function of the electrolysis time at 50 mA cm^{-2} current density of the electrode using a 1 sccm of CH_4.

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Conclusion

The BDD electrodes were effective in the process of electrochemical degradation of the solution containing the RO16 dye. It presented high performance considering the complete removal of the solution color, the TOC removal, and the degradation of aromatic compounds. The most efficient diamond electrode for this process was the film grown with the lowest percentage of CH_4. This behavior is associated with its highest diamond purity.

References

[1] Braga, N. A; Cairo, C.A.A; Almeida, E.C; Baldan, M. R; Ferreira, N.G. Diamond Related Materials 17, (2008), 1891-1896.