DEPOSITION OF MICRO AND ULTRANANOCRYSTALLINE DIAMOND ON RETICULATED VITREOUS CARBON FOR USE IN THE NITRATE ELECTROREDUCTION

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1. Introduction

Boron doped diamond (BDD) electrodes have been extensively used due to their higher electrochemical performance compared to vitreous carbon, graphite and platinum. The diamond growth by chemical vapor deposition (CVD) allows obtaining micro, nano and ultrananocrystalline films on various substrates depending on the gas mixture [1]. Currently, studies on nano and ultrananodiamond started to be more explored since they have been highlighted because of their excellent electrical, mechanical, thermal and biocompatible properties [2-4]. The combination of diamond and carbon substrate may produce a particular composite with good electrical conductivity depending on the carbon heat treatment temperature (HTT) as well as the diamond doping process. In this work, reticulated vitreous carbon (RVC) heat treated at 1000 and 2000 °C were used as carbon substrate for micro and ultrananocrystalline diamond growth and the nitrate electroreduction ability of these composites were demonstrated.

2. Experimental

RVC was processed using polyurethane foams with 70 pores per inch as a matrix for the poly(furfuryl alcohol) (PFA) resin impregnation. The impregnated foams were cured in an oven until 130 °C and then were heat treated at 1000 °C and 2000 °C (named RVC1000 and RVC2000). Micro and ultrananocrystalline diamond films were grown by hot filament chemical vapor deposition (HFCVD) technique for 18h under the pressure of 4 kPa, using 5 filaments of tungsten with 125 µm diameter and placed at 6 mm of sample top. Before diamond deposition, the RVC samples were prepared using seeding pretreatment to improve the diamond growth process. The substrates were immersed in a solution containing 0.25 µm of diamond particles dispersed in hexane solvent, followed by ultrasonic agitation for 2 h. Microcrystalline diamond films were grown on RVC1000 and RVC2000 with a gas mixture composed by 99.0 % H_2 and 1 % CH_4 and substrate temperature of about 800 °C. Ultrananocrystalline diamond were also grown on RVC1000 and RVC2000 with a gas mixture composed by 70.8% Ar, 28.3% H_2 and 0.88% CH_4 and substrate temperature kept at 680 °C. The boron doping was performed by an additional hydrogen line passing through a bubbler containing B_2O_3 dissolved in CH_3OH. The solution was prepared with a concentration of B_2O_3 dissolved in CH_3OH that correspond to B/C ratio of 30,000 ppm. The films were characterized by field emission scanning electron microscopy (FESEM), Raman spectroscopy and X-ray diffraction. All electrochemical experiments were performed in a conventional three-electrode cell, using the BDD/RVC and BDUND/RVC as working electrode, a Pt screen as the counter electrode and Ag/AgCl electrode as reference.

3. Results and Discussions

Micro and ultrananocrystalline diamond were grown with success on RVC stems. Figure 1 shows the XRD patterns of BDD and BDUND films grown on RVC heat treated at 1000 and 2000 °C. All samples present the carbon band (002) and diamond peaks (111), (220) and (311). The diamond peak (111) is more evident in BDD films due to its higher crystallite size while for BDUND film this peak is much broader. Figure 2 presents the Raman spectra of BDD and BDUND films which depict similar features to those obtained on the literature [2,5]. The characteristic bands for BDD films are the diamond peak at 1332 cm^{-1} in addition to the 500 and 1200 cm^{-1} bands related to the boron doping. The characteristic bands for BDUND films are the diamond peak shifted to lower wavenumbers (at around 1320 cm^{-1}) overlapped by the D band at 1350 cm^{-1}; the bands at 1150 and 1490 cm^{-1} related to the transpolyacetylene segments at the grain boundaries of the ultrananocrystalline diamond surface; the band at 1550 cm^{-1} assigned to G band; and the bands at 500 and 1220 cm^{-1}, related to the boron doping.

The electrochemical response of RVC, BDD/RVC and BDUND/RVC to nitrate was studied by cyclic voltammetry (CV) in 0.1 mol L^{-1} K_2SO_4 solution containing 0.01 mol L^{-1} KNO_3 as shown in Figure 3 and 4.

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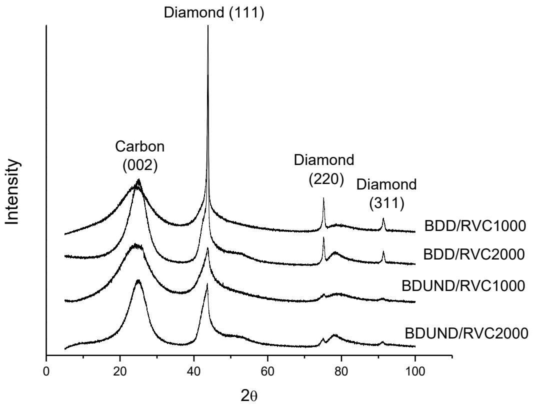

Fig. 1. *XRD patterns of BDD/RVC and BDUND/RVC composites*

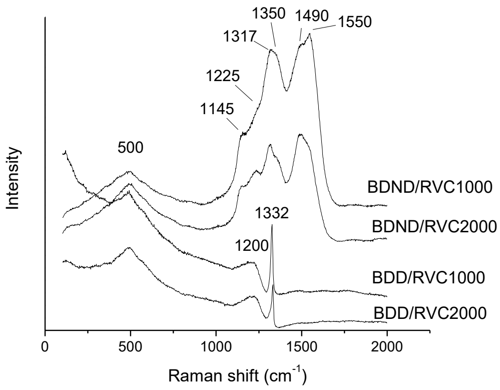

Fig. 2. *Raman spectra of BDD/RVC and BDUND/RVC composites.*

A comparison among RVC1000, BDD/RVC1000 and BDUND/RVC1000 electrodes for nitrate reduction (Figure 3) shows that in the presence of 0.01 mol L^{-1} KNO_3, the nitrate reduction clearly appears from -1.0 V for RVC1000, -0.65 V for BDD/RVC1000 and -0.75 V for BDUND/RVC1000 and they follow increasing the current when compared to the blank solution. Figure 4 presents the nitrate reduction for RVC2000, BDD/RVC2000 and BDUND/RVC2000 electrodes. The onset of the cathodic current in the presence of 0.01 mol L^{-1} KNO_3 appears at -0.85 V for RVC2000, -0.65 V for BDD/RVC2000 and -0.8 V for BDUND/RVC2000. These results indicate that both BDD and BDUND films improve the nitrate electroredution in comparison to RVC electrode, however, the BDD films are slightly better than BDUND films.

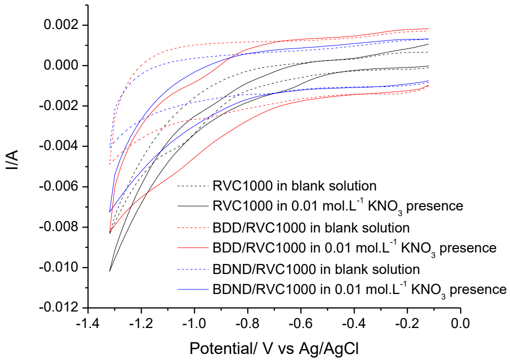

Fig. 1. *Cyclic voltammetries of RVC1000, BDD/RVC1000 and BDUND/RVC1000 in 0.1 mol L^{-1} K_2SO_4 (dotted line) and in presence of 0.01 mol L^{-1} KNO_3 (full line).*

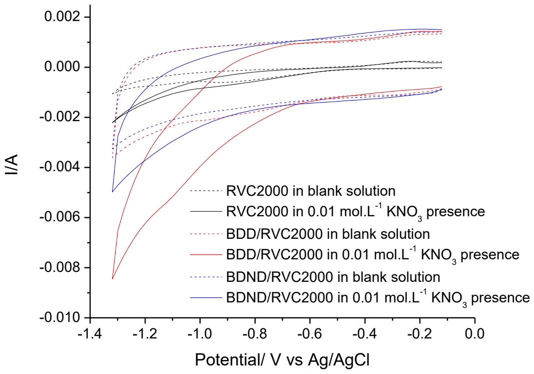

Fig. 2. *Cyclic voltammetries of RVC2000, BDD/RVC2000 and BDUND/RVC2000 in 0.1 mol L^{-1} K_2SO_4 (dotted line) and in presence of 0.01 mol L^{-1} KNO_3 (full line).*

4. References

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