Copper photoelectrodeposition onto boron doped diamond electrodes at different doping level to enhance nitrate electroreduction.

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ABSTRACT

Photoelectrodeposition of copper on boron-doped diamond films (BDD) was investigated. In this work, two different doped films were analyzed. Copper particles were deposited in the potentiostat mode and under UV irradiation. The BDD film as-grown and the BDD film modifed with Cu (Cu/BDD) on the surface were characterized by Raman Spectroscopy and Scanning Electron Microscopy (SEM) respectively. These electrodes were tested as electrocatalysts for nitrate reduction in Britton-Robinson buffer solution (pH=3). Electrochemical measurements showed that the electrode with high doping level displayed the best electrocatalytic activity.

INTRODUCTION

Nitrate electroreduction is one of the methods used to abatement of these ions from the polluted waters since it offers low cost operation. Besides, this technique is considered a clean process and highly effective [1]. The mechanism for the nitrate electroreduction is very complex and depends strongly on the experimental parameters such as the pH, the supporting electrolyte and the choice of the electrode material [2-4]. In this sense, boron doped diamond (BDD) appears as an excellent electrode to study the nitrate reduction due to its outstanding electrochemical features such as the wide potential window in aqueous solutions and the weak adsorption for the most types of molecules [5, 6]. It is noteworthy that is very important to reduce the overpotential for the nitrate reduction in aqueous media, since its reduction occurs near the water reduction. One way of achieving this is by modifying the electrode surface with catalytic materials. In particular, this can be achieved by depositing copper particle on the BDD surface, which exhibits the best electrocatalytic activity considering the kinetics for the nitrate reduction process [7]. Taking into account the BDD semiconducting characteristic, its photoactivity may be explored. So, the photo-assisted metal deposition method is very useful for the preparation of efficient electrode material [8]. The diamond in its natural state is considered a semiconductor with band gap energy of 5.5 eV. Due to its extremely wide band gap and the fact of the conduction band edge is located at a very negative potential (-4.0 V versus SHE (Standard Hydrogen Electrode)), the photogenerated electrons have extremely high reducing power [9]. So, the diamond serves as both a source of electrons for reduction of the ion to be deposited and as a substrate for deposition process. Thus, the aim of this work is to investigate the photoelectrodeposition of copper on semiconducting BDD films with different doping levels. Furthermore, these modified electrodes were applied to nitrate electroreduction, since the copper catalyses this process.

EXPERIMENTAL DETAILS

The films were grown by hot filament-assisted chemical vapor deposition (HFCVD) technique using the gas mixture of 1/99% of the CH_4/H_2 with a pressure of 50 Torr and substrate temperature around 800ºC, during 16 h. The films were deposited on the silicon substrate after seeding pre-treatment [10]. Boron source was obtained by an additional hydrogen line passing through a bubbler containing B_2O_3 dissolved in methanol with a controlled B/C ratio that led to films with different doping level of 10^{19} and 10^{21} atoms.cm^{-3}, denominated as electrode E1 and electrode E2 respectively.

Electrochemical measurements were made using the Autolab PGSTAT 302 equipment with a three-electrode cell. The geometric area of the diamond films in contact with the electrolyte was 0.13 cm^2. A platinum mesh served as a counter electrode and Ag/AgCl/KCl$_{(sat)}$ was used as the reference electrode. Prior to the photoelectrodeposition, the films were exposed under UV irradiation for 2h to promote the oxygen functional groups that serves as anchor points for Cu deposited improving the interfacial adhesion between BDD films and the metal coating [13]. The photoelectrodeposition of Cu particles on diamond films was performed in the potentiostatic mode, at a fixed potential of -0.6 V for a time of 10 min, in a 1 mmol L^{-1} CuSO$_4$, 50 mmol L^{-1} H$_2$SO$_4$ aqueous solution, under UV irradiation. The light source was a home made system, composed by a set of five commercial lamps (Philips TUV 30 W/G30T8) placed in a closed box. The UV irradiation at the electrode position was 12 W/m^2 measured by a radiometer. Before (30 min) and during the photoelectrodeposition, the solution was purged with N$_2$. The Cu modified diamond films morphology was verified from the scanning electron microscopy (SEM) images using a Jeol JSM-5310 microscope. Nitrate reduction experiments were monitored by the linear sweep voltammetry using 0.01 mol L^{-1} KNO$_3$ + 0.001 mol L^{-1} Britton-Robinson (BR) buffer (pH=3).

DISCUSSION

Characterization of BDD films – Raman Measurements

Figure 1 shows the Raman´s scattering spectra of the electrode E1 and the electrode E2. The characteristic Raman peak close to 1332 cm^{-1}, which corresponds to the vibration of a diamond first-order phonon, confirmed the quality of these BDD films. The effect of boron doping is reflected in the spectral features. The peak of the diamond (1332 cm^{-1}) shifted to lower energies due to tensions caused by boron incorporation in the diamond films. Besides, the diamond peak decreased in intensity due to the high B content in such films. In addition, there is the appearance of the two bands located at 500 cm^{-1} and 1220 cm^{-1}. The band at 1220 cm^{-1} is attributed to the reticular distortion by boron insertion in the crystal structure of the diamond. The broad band at ~1220 cm^{-1} feature increases with the B concentration increase. The band at around 500 cm^{-1} is assigned to the vibration modes of the boron pairs [11]. The boron concentration in the diamond films was estimated from the fitting of 500 cm^{-1} peak using a combination of Gaussian and Lorenzian lines [12]. The acceptor concentrations were evaluated around 10^{19} and 10^{21} boron atoms cm^{-3} for the electrode E1 and the electrode E2

electrodes, respectively. The highest doping level of the electrode E2 is clearly observed in figure 1 where the band at 1220 cm^{-1} is higher than the diamond peak.
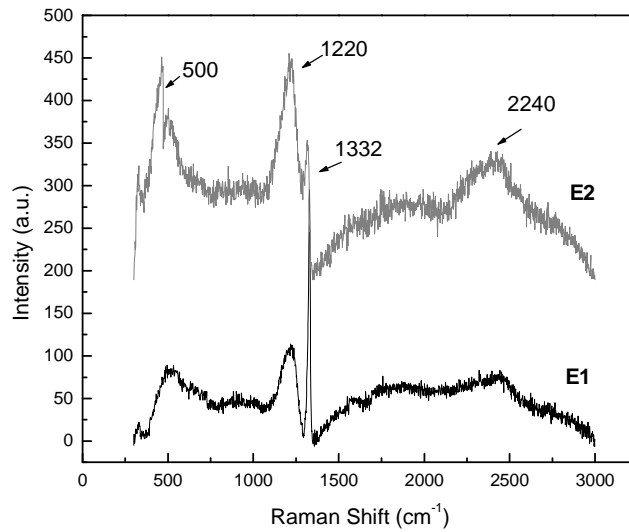
Figure 1. Raman spectra of E1 and E2 BDD electrodes.

## Copper particles photoelectrodeposition

SEM analysis of the electrode E1 and the electrode E2 films after the Cu photoelectrodeposition are shown in figure 2 as images (a) and (b), respectively. The surface modification with Cu particles resulted in a morphology composed of rounded grains distributed throughout the surface of both films, with high density and uniformness of Cu. These deposits may be explained due to the semiconductor character of such films. Firstly, the BDD surface presents high diamond purity where the conductivity is due to the boron excess at the top of its valence band. Therefore, the photoassisted process by UV irradiation generated additional electrons at the conduction band that could participate in the Cu electroreduction. In addition, the positive holes at the valence band may oxidize the water to molecular oxygen or hydroxyl radicals. Besides, the BDD is a semiconductor with a wide band gap. This process is improved due to this large band gap, where the recombination of the electrons is lower compared to that of conventional semiconductors [14]. In this way, this excess of electrons enhanced the Cu deposition. In a different way, previous work showed that for BDD electrode in the absence of UV irradiation, the copper deposit was obtained only at the diamond grain boundaries and/or in dispersed places of the grain faces [13].
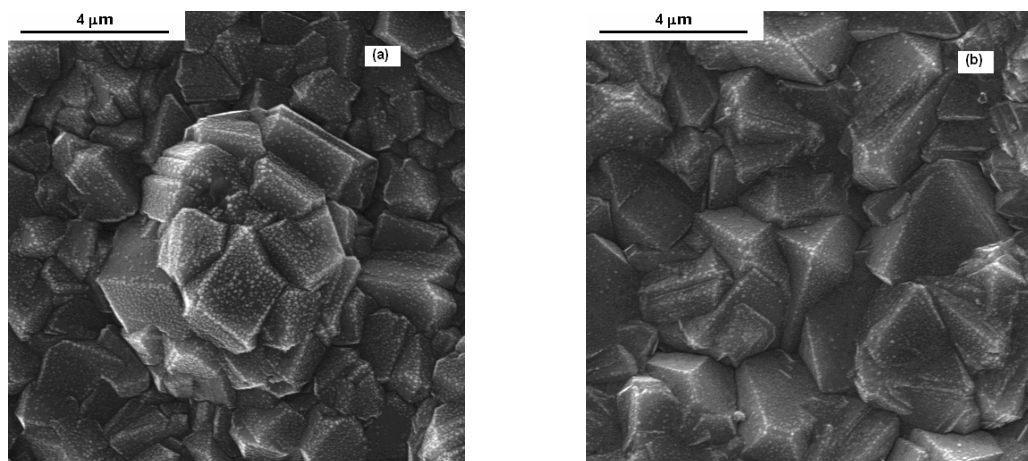
Figure 2. SEM images of E1 (a) and E2 (b) electrodes after Cu particle photoelectrodeposits.

Nitrate Electroreduction

These modified films were used to evaluate their performance in the nitrate reduction. Figure 3 presents linear sweep voltamograms in the presence of nitrate for as-grown and Cu/diamond films. For both electrodes, the cathodic currents for buffer BR are associated to the water reduction.
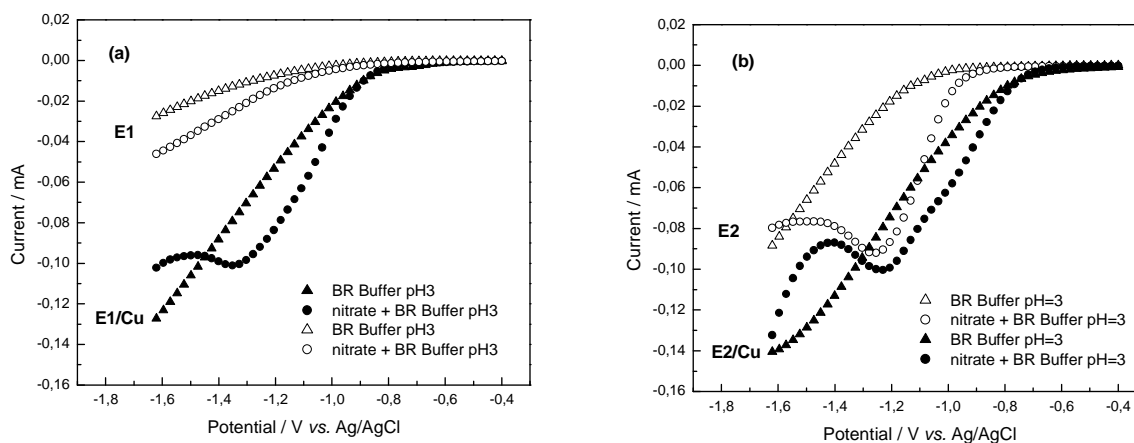
Figure 3- The response of diamond electrodes for 0.001 mol L^{-1} Britton Robinson buffer and for nitrate reduction in solution of 0.01 mol L^{-1} KNO$_3$ + 0.001 mol L^{-1} Britton Robinson buffer. (a) E1 and E1/Cu; (b) E2 and E2/Cu electrodes.

From the above results, it is possible to observe that Cu deposited on diamond surface catalysed the electroreduction of nitrate for both electrodes. The nitrate electroreduction is a very complex process. Several products are possible depending on the experimental conditions such as the pH and the applied potential. In this work, only one cathodic peak is observed around -1.25 V for E1/Cu film, suggesting that nitrate reduction to ammonia is taking place at this potential. In Figure 2 (b), for E2/Cu, it is possible to observe the

appearance of a slight new peak at around -1.0 V associated to the nitrate reduction into hydroxylamine followed by the ammonia peak. This behavior may be explained by the highest conductivity of E2 electrode. These reduction processes were already observed by Aouina *et al* for the electroreduction of nitrate at a copper electrode in the neutral solution [15]. In addition, the stability of Cu particles on these films was evaluated from successive linear sweep voltammetry measurements for the nitrate reduction. The measurement reproducibility was obtained, indicating that the copper particles were consolidated on the electrode surface. This behavior can be explained by the Cu particle deposition on the diamond faces and the presence of oxygenated groups on the BDD surface induced by the UV pretreatment that serves as anchor point for Cu photoelectrodeposit.

CONCLUSIONS

This study showed that the copper photoelectrodeposition process on semiconducting diamond surface can be a good alternative for the preparation of modified electrode at different doping levels. By applying UV irradiation, the copper photoelectrodeposited presented high density and were uniformity distributed all over the crystal faces. This behavior was attributed to the generated additional electrons at the conduction band, where the recombination process on BDD is low and, consequently, ensured an increase in the density of copper deposits. Concerning the nitrate reduction process, the activity of Cu on the BDD was evident, where for E1/Cu one cathodic peak was observed corresponding to ammonia peak while for E2/Cu electrode two cathodic peaks associated to the nitrate reduction were found. The first one refers to hydroxylamine and the second one to the ammonia peak. Besides, these electrodes showed reproducible measurements for nitrate reduction.

ACKNOWLEDGMENTS

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