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Anodic and cathodic pre-treatment effects on BDD surface to deposit copper nanoparticles applied to nitrate reduction

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ABSTRACT

The influence of anodic and cathodic pre-treatment on boron doped diamond (BDD) surface for copper (Cu) electrodeposition was studied to assess Cu particle consolidation on BDD electrode. These modified electrodes were applied to study the nitrate electrochemical reduction process. The obtained results showed that the BDD surface cathodically treated presented high Cu particle density as well as even distribution on the electrode surface after the electrodeposition process. For samples anodically treated the electrodeposited Cu was dispersed with lower particle density. This behavior was attributed to a high electrode conductivity imposed by the cathodic pre-treatment leading to an increase in the BDD surface hydrogenation. Therefore, one can conclude that for electrochemical nitrate reduction the anodically treated BDD has a better reproducibility. This response is attributed to the Cu particle consolidation on BDD electrode due to the oxygen surface terminations induced by the anodic pretreatment.

INTRODUCTION

Nowadays, nitrate represents a critical issue for fresh water contamination as well as coastal waters due to poor sanitation and limited waste water treatments [1]. Moreover, the use of nitrogen-based compounds for a wide number of applications, such as in agriculture as an integral part of fertilizers and insecticides, in chemical synthesis as precursors of a large variety of chemicals, and in the food industry as preservers, flavoring, and disinfectants corroborates to increase the contamination problem [2]. These considerations give us a valid basis to develop systems to perform quantitative analysis, monitoring and tertiary treatment for nitrate ions in water. In the last thirty years electrochemical methods have been extensively studied because it can be considered as a clean one once the reactions main reagent is the electron [3-5]. In this sense, boron doped diamond (BDD) electrodes appear as an alternative solid material with singular electrochemical properties [6,7] to nitrate reduction applications due its wide potential window and low background current such electrode avoids adsorption problems of reagents and/or products. The surface modification of solid electrodes represents an important strategy by promoting selectivity in such process improving the electrode properties for many

electrochemical reactions. Taking into account the modified BDD electrodes, the electrochemical deposition offers an easy and rapid alternative process to produce particle modified electrode to detect nitrate. Thus, this work presents a new treatment based on the effects of anodic (AT) and cathodic (CT) pre-treatment on BDD surface aiming to improve the Cu particle consolidation on BDD surface during its electrodeposition, since that Cu has demonstrated to be the best electrocatalysts considering the kinetics to reduce the nitrate [8].

EXPERIMENTAL DETAILS

BDD films were grown utilizing hot filament-assisted chemical vapor deposition (HF-CVD) technique at 1050 K from 1.0% vol. CH_4 in H_2/CH_4 mixture at a total pressure of 6.5×10^3 Pa. The films were deposited on silicon substrate after seeding pre-treatment [9] during 7 hours. Boron was obtained from H_2 forced to pass through a bubbler containing B_2O_3 dissolved in methanol. The B/C ratio used corresponds to the acceptor densities of around 10^{21} cm^{-3} estimated from Raman measurements. Scanning Electron Microscopic (SEM) top view images of Cu modified BDD films were obtained with a Jeol equipment JSM-5310. Sessile drop contact angle measurements were carried out on a Krüss Easy Drop system by calculating the contact angle (θ) between the diamond layer and liquid drop high-purity de-ionized water at room temperature and atmospheric pressure. Electrochemical measurements were made using Autolab PGSTAT 302 equipment with a three-electrode cell. The geometric area of the BDD films in contact with the electrolyte was 0.27 cm^2 . A platinum coil wire served as a counter electrode and $\text{Ag}/\text{AgCl}/\text{KCl}_{(\text{sat})}$ electrode was used as the reference electrode. The cathodic and anodic pre-treatments were performed using the -3 V and +3 V, respectively, during 30 min in solution of $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. The electrodeposition of Cu particles on BDD films was performed under potentiostatic mode, at a fixed potential of -0.6 V for a time of 60 s, in solution of $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ support electrolyte containing $0.001 \text{ mol L}^{-1} \text{ CuSO}_4$. Nitrate reduction experiments were monitored by linear sweep voltammetry (LSV) using a $0.1 \text{ mol L}^{-1} \text{ KNO}_3 + 0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution.

DISCUSSION

Cathodic and anodic pre-treatment

The figure 1 (a, b and c) shows the contact angles for the three electrodes named BDD-AG (as-grown), BDD-CT and BDD-AT with values of 62.9, 71.7 and 16.9°, respectively. It is clearly observed that the BDD-AG electrode already presents an H-terminated surface and the CT promoted only a slightly increase on its hydrophobicity. Otherwise, an abrupt decrease in the contact angle value is observed for BDD sample after the AT. This surface presents more oxygen containing functional groups that serve as active centers of water wetting.

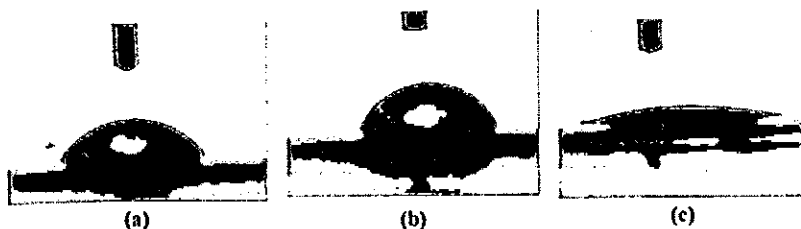


Figure 1. Contact angles images for BDD electrodes: (a) BDD-AG; (b) BDD-CT; (c) BDD-AT.

The influence of CT and AT pre-treatment may also be observed by the voltammetric characterization of Cu/Cu(II) system from cyclic voltammograms at 100 mV s^{-1} in CuSO_4 solution on the three BDD electrodes showed in figure 2.

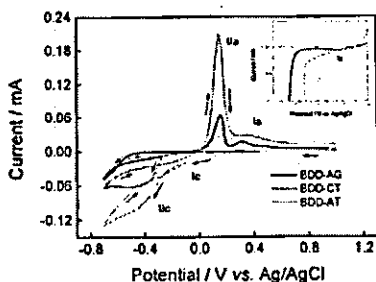
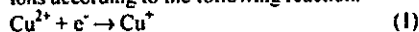
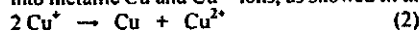


Figure 2. Cyclic voltammetry responses of BDD-AG, BDD-CT and BDD-AT electrodes in solution of $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ support electrolyte containing $0.001 \text{ mol L}^{-1} \text{ CuSO}_4$.

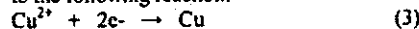
The potential sweep started at 1.0 V and during the negative potential scan a plateau of Cu cathodic current around $+0.21 \text{ V}$ was observed for AG, CT and AT BDD electrodes. The initial cathodic current corresponding to I_c process is assigned to the reduction of Cu^{2+} to Cu^+ ions according to the following reaction:



It is suggested that the reaction (1) is followed by disproportionation of the produced Cu^+ ions into metallic Cu and Cu^{2+} ions, as showed in the reaction (2).



The I_c process is immediately accompanied by I_{lc} process as the response to direct reduction of Cu^{2+} ions (from Cu^{2+} ions of bulk solution and those from reaction (2)) to metallic Cu according to the following reaction:



These reduction processes have already been observed by Grujicic and Pesic [10] for Cu electrodeposition on vitreous carbon electrode. It is interesting to point out that the cathodic current plateau regarding $\text{Cu}^{2+}/\text{Cu}^+$ process is highest for BDD-AT electrode, indicating a more

favorable energy condition for this process, probably due to surface functionalization with oxygen.

For the three presented voltammograms in Fig. 2, the onset of this reduction reaction (3) was more negative than its equilibrium for Cu/Cu^{2+} redox potential, assigning the influence of the electrode surface. Leading the sweep reversal at -0.7 V, the current became anodic in narrow potentials around 0.9 V for BDD-AG and BDD-CT electrodes, while for BDD-AT electrode this process begins at more negative potential. The first anodic peak, named Ia is typical for a bulk Cu stripping, concerning the inverse way of reaction (3). The second anodic peak, clearly present for BDD-AG and BDD-CT is associated to the dissolution of other Cu phases, characterized by the reverse of reaction (1). For the BDD-AT electrode, the behavior is rather different. The first anodic peak also appears, representing the smallest Ia peak among those for the three electrodes. Also, this peak is followed by a slightly decrease of the anodic current that is kept during the whole anodic scan and do not tend to zero after the total dissolution process, as expected. This current refers to the dissolution of other phases of copper formed with different energies on such electrode such as different crystalline orientations or even those that eventually were bonded to some oxygen present on anodically BDD treated.

Copper particles deposition and nitrate reduction

The morphology of the Cu deposited as presented in figure 3, where images (a) and (b) refer to BDD-CT and BDD-AT, respectively. The results showed that BDD-CT (a) exhibits a higher density and an even distribution of Cu particles on the electrode surface, while for the BDD-AT (b) the electrodeposition was unevenly distributed with lower density. Also, the particles on image (a) are clearly smaller than the ones on image (b). This deposition pattern may be attributed to a better conductivity of the electrode that was promoted by the cathodic treatment associated with the surface hydrogenation process which was also confirmed by the contact angle measurements. Conversely, for BDD-AT, in addition to its conductivity decrease, the oxygen amount on the electrode surface also blocks the transfer reactions leading to the Cu^+ formation as discussed above.

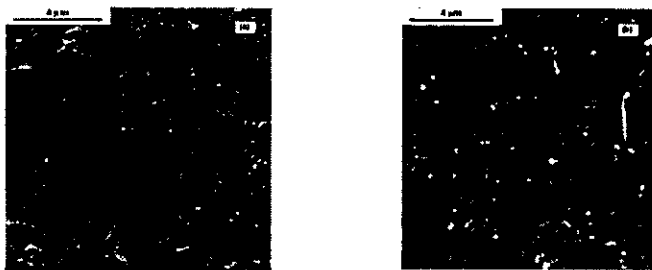


Figure 3. SEM images of BDD-CT (a) and BDD-AT (b) electrodes after Cu particle electrodeposits.

After this Cu particle size and density characterizations with respect to the BDD surface treatment the next step was to assess its differing analytical properties to nitrate reduction.

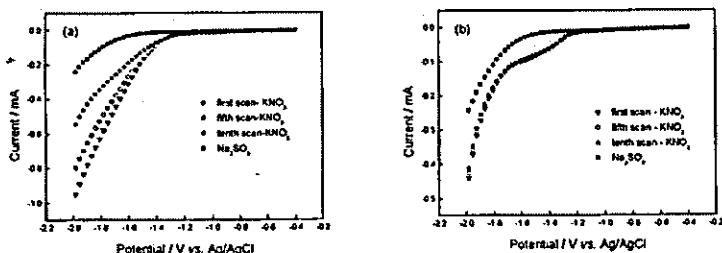


Figure 4- The response of diamond Cu modified electrodes for $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ and for nitrate reduction in solution of $0.1 \text{ mol L}^{-1} \text{ KNO}_3 + 0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$. (a) BDD-CT and (b) BDD-AT.

The nitrate reduction using may be observed from LSV measurements present in figure 4 (a) and 4 (b) for BDD-CT and BDD-AT electrodes, respectively. For both electrodes the cathodic current for Na_2SO_4 is associated with H_2O reduction and H_2 evolution. Nonetheless, when nitrate is added in the solution an additional cathodic current higher than the previous one starts to build up (around -1.2 V) and increases significantly as the potential becomes more negative, for both electrodes.

Significant observations may be done in the nitrate reduction process in subsequent LSV measurements. Concerning the BDD-CT electrode although in the first scan a highest cathodic current is produced this response is not reproducible. As shown in figure 4a the cathodic current decreases as scans progress, which indicate that the copper particles are not consolidated on the electrode surface. Conversely, for the BDD-AT electrode (figure 4b) the reproducibility is clear for the ten exposed scans and the nitrate reduction process is observed as a separate "shoulder" around -1.4 V . In order to explain this effect it is necessary to take into consideration that the oxygen presence influences on the Cu deposits. Recently, Córdoba and Odén [11] discussed the electroless process of the deposited Cu films on carbon nanofibers (CNF). They pointed out that the poor adhesion to copper on carbon may be improved from pretreatments to form carboxylic, carbonylic and hydroxylic groups on their nanofiber surfaces. For the electroless process, they considered that these groups can act as anchor points for Cu-clusters improving the interfacial adhesion between CNF and the metal coating.

Similarly, as a result of this work we believe that the high amount of oxygen content on BDD-AT electrode presents functional groups such as " $\text{C}=\text{O}$ ", " $\text{C}-\text{O}$ " and " $\text{C}-\text{OH}$ " [12] which may promote some kind of Cu anchorage in our BDD electrode make it very attractive for nitrate reduction.

CONCLUSIONS

We have demonstrated that a surface pre-treatment of the BDD electrode can be a good alternative method to consolidate copper particles from electrodeposition process on its surface. Cyclic voltammetry results showed two Cu cathodic processes (Ic and IIc) in all BDD electrodes. However, a higher cathodic current plateau related to Ic process was observed for BDD anodically treated. The SEM images also showed the singular Cu particles morphology for BDD-AT surface with low density and dispersed particles compared to the BDD-CT electrode, but in good agreement with its lowest Cu dissolution peak. Nonetheless, for nitrate reduction process, the BDD-AT electrode presented the best response and reproducibility. This effect was attributed to the oxygen functionalities induced by the pretreatment on its surface that works as an anchor for Cu particles.

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