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Nitrate Removal by Electrolysis Using Cu/BDD Electrode Cathode

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Copper particles were deposited in the potentiostat mode and under UV irradiation on the boron doped diamond (BDD) surface. The copper deposited presented high density and uniformity all over crystal faces. This behavior may be associated with its semiconductor character that promoted additional photogenerated electrons enhancing the copper reduction reaction. This modified electrode was used as a cathode electrode on the studies of the nitrates removal from aqueous solutions by electrolysis in an undivided electrochemical cell and BDD as an anode electrode. The nitrate reduction was analyzed at three differents initial pH (neutral, acid and basic). The nitrate reduction rate did not increase linearly as a function of current densities using potassium sulphate as the electrolyte (neutral pH). In the present experiment, the optimum current density was 20 mA/cm^2. The nitrate reduction decreased from 150 to 63.8 ppm. Regarding to the influence of initial pHs used, it could be conclude that high value of pH favours the nitrate electroreduction. This result may be associated with the higher competition between the H^+ and the NO_3^- ions by electrons on the cathode surface, causing a decrease in the efficiency of electrolysis.

Introduction

Nowadays, cleaner technologies are required in the treatment of polluted water effluents. At this point, electrochemical process has shown to be highly effective and inexpensive alternative technique for this purpose since the principal reagents are the electrons, and thus presents environmental compatibility. In particular, nitrate has been considered an important nitrogen inorganic contaminant of soil and natural waters due to its capability of carrying not only on the surface but it also penetrates the soil, thus contaminating large areas [1]. Several groups have focused their efforts in preparing nitrate electrolysis, since its electroreduction depends on the electrode material, current density, electrolyte concentration and pH [2, 3]. In this sense, boron doped diamond (BDD) has been reported to be an excellent electrode to study nitrate reduction due to its outstanding electrochemical features such as: wide potential window in aqueous solutions and weak adsorption for most types of molecules [4]. It is known that its behavior can be improved from surface modifications with metallic particles deposition. This modification is responsible to increase the electrocatalytic activity of the electrode and, consequently, increase the sensitivity and selectivity of the process. To reduce the nitrate ion, several metals have been used [5, 6, 7], but Cu is considered one of the best electrocatalytic metals considering the kinetics for nitrate reduction process. In this context, the main aim of the present work is to modify the BDD surface with Cu particle using photoelectrodeposition as a method for obtaining Cu/BDD electrode, in order to analyze their performance as a cathode with respect to nitrate electroreduction. Likewise, the influence of current density and pH in the nitrate electrolysis were studied.

Experimental Procedure

The BDD electrode was grown on Ti substrate by hot filament chemical vapor deposition (HFCVD) technique with dimensions of 10 mm x 10 mm x 0.5 mm and with the following growth parameters: 780 ^{o}C, 50 Torr, 14 h and gas mixture 1/99 % of CH_4/H_2. Boron source was obtained by an additional hydrogen line passing through a bubbler containing B_2O_3 dissolved in methanol. From Raman's measurements the doping level was estimated to approximately 10^{21} atoms cm^{-3}. Electrochemical measurements were carried out using a standard three-electrode cell. A platinum wire served as a counter electrode and Ag/AgCl/KCl$_{(sat)}$ was used as reference electrode. Prior to the photoelectrodeposition, the films were exposed under UV irradiation during 2h to promote the oxygen functional groups that serve as anchor points for Cu deposited thus improving the interfacial adhesion between BDD films and the metal coating. The photoelectrodeposition of Cu particles on diamond films were performed under potentiostatic mode, at a fixed potential of -0.6 V during 10 min in a 50 mmol l^{-1} $NaClO_4$ + 1 mmol l^{-1} $CuSO_4$ aqueous solution, under ultra-violet (UV) irradiation. The light source was a 30 W UV deuterium lamp. The Cu modified diamond films morphology was verified from scanning electron microscopy (SEM) images using a Jeol JSM-5310 microscope. For the nitrate electrolysis experiments, about 300 mL of the nitrate solution prepared with 150 ppm KNO_3 + 0.1 mol L^{-1} K_2SO_4 was electrolyzed during 5 h. At different intervals, 1 mL samples were withdrawn from electrochemical cell and the nitrate anion decay was analyzed by ion chromatography using Metrohm IC-850 equipment (column, METROSEP A SUPP 5; mobile phase, 3 mmol L^{-1} Na_2CO_3 + 1 mmol L^{-1} $NaHCO_3$). Different current density was applied under galvanostatic control at 10, 20, 40, 60, 100 mA/cm^2. The effect of three different pH solutions (acid, neutral and basic) was evaluated at a fixed current density of 20 mA/cm^2.

Results and discussion

Figure 1 shows the Raman´s scattering spectrum of the BDD film. The peak close to 1332 cm^{-1} corresponds to the vibration of a diamond first-order phonon, and confirms the quality of this BDD film. 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 diamond lattice, and this peak decreased in intensity due to its high B content. The appearance of the two bands located at 500 cm^{-1} and at 1220 cm^{-1} is attributed to B-B vibrations and to B-C vibrations, respectively [8]. More recently, Niu et al. [9] have discussed the electronic and the vibrational properties of heavily BDD. They concluded that the 500 and ~1220 cm^{-1} bands are both superposed bands, including not only C vibrations but also B-B vibrations and B-C vibrations, respectively. The boron concentration in diamond film was estimated from the fitting of 500 cm^{-1} peak using a combination of Gaussian and Lorenzian lines [10]. The acceptor concentrations were evaluated at around 10^{21} boron atoms cm^{-3} for this electrode. The high doping level of this film is clearly observed in Figure 1 where the band at 1220 cm^{-1} is higher than that of the diamond peak not to mention its evident second order feature at around 2500 cm^{-1}. The SEM image (Figure 2A) of the diamond film deposited on the Ti substrates shows that the BDD film grew with a continuous and uniform surface morphology covering the whole substrate without delamination or cracks, characterized by well-shaped microcrystalline grains. It presents sharp facets and crystallographic orientation varying between <111> and <200>.

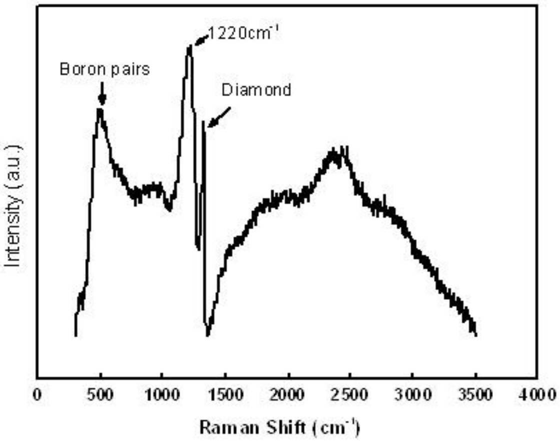

Figure 1: Raman spectrum of the BDD electrode.

Figure 2B shows the surface modification with Cu particles resulted in a morphology composed of rounded grains distributed throughout the surface for the BDD film.

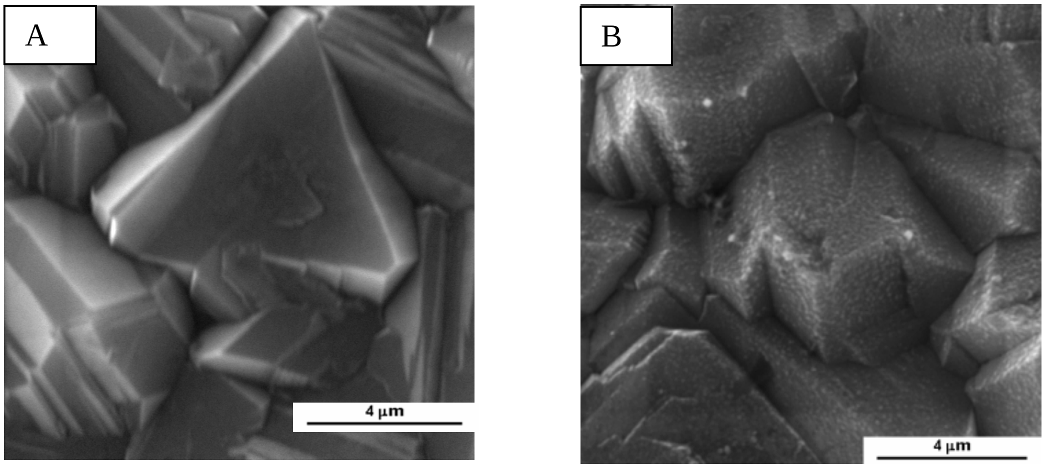

Figure 2: SEM images of BDD electrode before (A) and after (B) Cu photoelectrodeposits.

It presents great density and good uniformness of Cu particles on the electrode surface that can be associated to the photoassisted process by UV irradiation, which generates additional electrons in the conduction band that may participate in the Cu electroreduction. Furthemore, BDD represents a wide band gap semiconductor. This process is improved due to the large BDD band gap, where the recombination of the electrons is lower compared to that of conventional semiconductors [11]. In this way, these additional electrons enhanced the Cu deposition. This modified film was used to evaluate its performance in nitrate electroreduction.

The nitrate electrolysis was carried out using BDD as anode and Cu/BDD as cathode with a geometric area of the diamond films in contact with the electrolyte was 4.15 cm^2. The electrolysis assays were performed at different current densities of 10, 20, 40, 60 and 100 mA cm^{-2} by using 0.1 mol L^{-1} K_2SO_4 + 150 ppm KNO_3. Figure 3 reports the change of nitrate concentration as a function of time for different current densities.

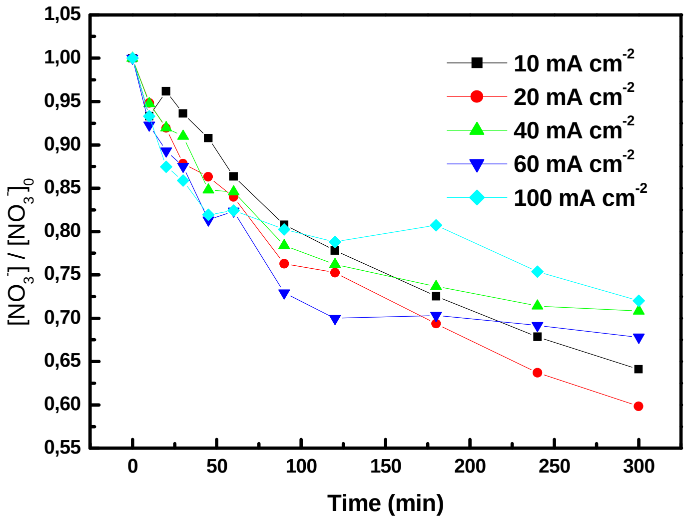

Figure 3: The variation of nitrate removal rate at different current densities (initial concentration 150 ppm, neutral pH).

The combination of the BDD anode and Cu/BDD cathode enabled good performance for electrochemical nitrate reduction at current densities ranging from 10 to 100 mA/cm^2. The nitrate reduction rate did not increase linearly as a function of current densities. The nitrate reduction rate increased with increasing current density from 10 to 20 mA/cm^2, but decreased with increasing the current density from 40 to 100 mA/cm^2. This behavior may be due to the large power consumption by the side reaction of hydrogen evolution, which competes with nitrate reduction. The optimum current density in the present experiment was 20 mA/cm^2 in which the nitrate concentration decreased from 150 to 63.8 ppm. It is interesting to point out that the pHs of all treat solutions increased to 5-11 in 300 min, mainly due to the reactions forming hydroxyl ions during the electrochemical reduction of nitrate. According to the literature, the proposed mechanism for nitrate reduction compatible with the increase in the pH is shown below [12].

$$NO_3^- + H_2O + 2\,e^- \leftrightarrow NO_2^- + 2\,OH^- \qquad (1)$$

$$NO_3^- + 6\,H_2O + 8\,e^- \leftrightarrow NH_3 + 9\,OH^- \qquad (2)$$

$$NO_2^- + 5\,H_2O + 6\,e^- \leftrightarrow NH_3 + 7\,OH^- \qquad (3)$$

$$NO_2^- + 2\,H_2O + 3\,e^- \leftrightarrow \frac{1}{2}N_2 + 4OH^- \qquad (4)$$

It is known that the nitrate reduction mechanism strongly depends on the electrolyte pH [13]. Taking into account this behavior, the nitrate removal using the modified Cu/BDD film, was performed considering the three different initial pHs (acid, neutral and basic) and using current density of the 20 mA/cm^2. Fig. 4 shows the decay of the nitrate as a function of time using different initial pHs.

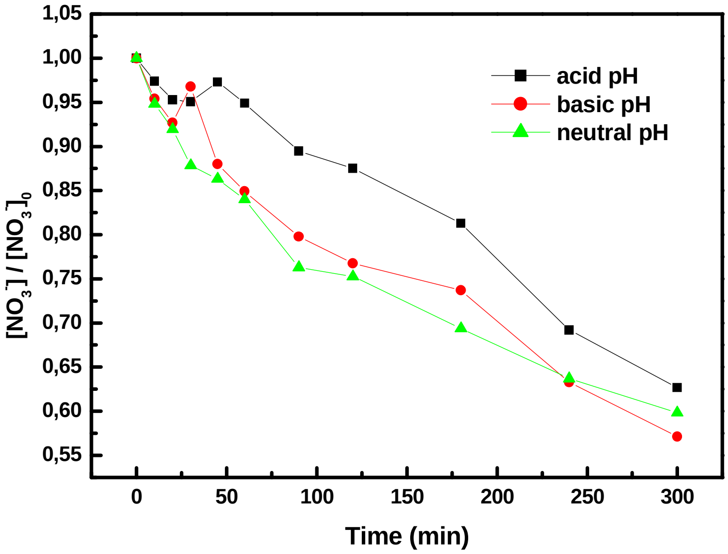

Figure 4: The variation of nitrate removal rate as a function of initial pH (initial concentration 150 ppm, current density 20 mA/cm^2).

Preliminary results showed no significant influence on nitrate reduction using neutral and basic pH. It is observed that the reduction rate slightly increased with increasing the pH of the solution. On the other hand, the worst nitrate reduction rate in acid pH may be associated with a high H$^+$ concentration that compete with the NO_3^- ions by electrons on the cathode surface, causing a decrease in the efficiency of electrolysis.

Conclusion

This study reported that the copper photoelectrodeposition process on semiconducting diamond surface can be a good alternative for the preparation of modified electrode. By applying UV irradiation, the copper photoelectrodeposits presented high density and uniformity 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. The combination of the Cu/BDD cathode and BDD anode was suitable for electrochemical reduction of nitrate in an undivided cell. The optimum current density obtained in this work was 20 mA/cm^2 and basic pH. The nitrate reduction rate slightly decreased with acid pH value, probably due to competition between the H$^+$ and the NO_3^- ions by electrons on the cathode surface.

Acknowledgments

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