Nitrate removal by electrolysis using Cu/BDD electrode cathode

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Nowadays, cleaner technologies are been required in the treatment of polluted water effluents. In this context, electrochemical process has shown to be highly effective and inexpensive alternative technique for this purpose. In particular, nitrate has been considered an important environmental 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. Several groups have focused their efforts in preparing electroreduction (1). 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 (2). It is known that its behavior can be improved from surface modifications with metallic particles deposition. In this context, Cu is considered one of the best electrocatalytic metals considering the kinetics for nitrate reduction process. *The* aim *main of* the present work is to modify the BDD surface with *C*u 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. The films were grown by hot filament-assisted chemical vapor deposition (HFCVD) technique 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. The doping level corresponds to the acceptor densities of around 10^{21} atoms cm^{-3} estimated from Raman's measurements. 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 the 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 for a time of 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 deuterium lamp. 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 for 5 h. At different intervals, 1 mL samples were withdrawn from the electrochemical cell and it was analyzed by ion chromatography. Different current density was applied under galvanostatic control at 10, 20, 40, 60, 100 mA/cm^2. Three different pH solutions (acid, neutral and basic) were used. The Figure 1 shows the Raman´s scattering spectrum of the BDD film.

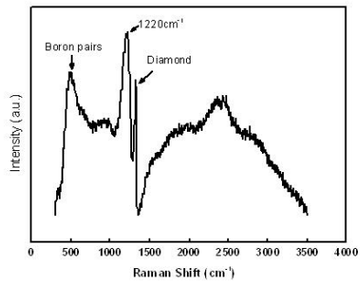

Figure 1: Raman spectrum of the BDD electrode.

The peak close to 1332 cm^{-1} corresponds to the vibration of a diamond first-order phonon, confirmed the quality of this BDD film. 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. SEM image (Figure 2A) of the diamond film deposited on the Si 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 2B shows the surface modification with Cu particles resulted in a morphology composed of rounded grains distributed throughout the surface for the BDD film.

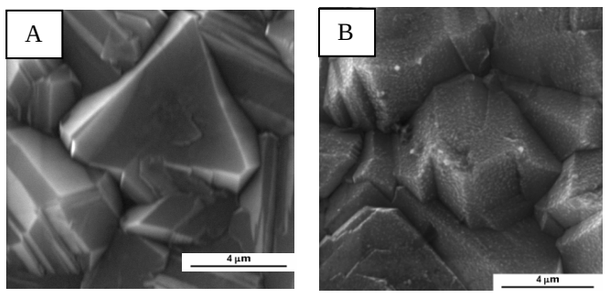

Figure 2: SEM images of BDD electrode before (A) and after (B) Cu photoelectrodeposits.

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 optimum current density in the present experiment was 20 mA/cm^2 in which the nitrate concentration decreased from 150 to 63.8 ppm. Considering the different initial pHs and using current density of the 20 mA/cm^2, preliminary results showed no significant influence on nitrate reduction. It is observed that the reduction rate slightly increased with increasing the pH of the solution.

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References

[1] Archa, Surinder K. Sharma, Ranbir Chander Sobti, E-Journal of Chemistry, 9(4), 2012.
[2] V. Georgeaud, A. Diamand, D. Borrut, D. Grange, M. Coste, Water Science & Technology, 63.2, 2011.