

## Diamond electrodes for wastewater treatment

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Submitted on July 7, 2015; Revised on October 28, 2015

**Abstract.** Boron doped nanocrystalline diamond films (BDD) immobilized with photosensitive molecules have been studied as electrode material for reduction of nitrate in waste water. This process is one of the most important goals of the modern electrochemistry. The diamond thin films were deposited on silicon substrate by Hot Filament Chemical Vapour Deposition (HFCVD) technique. Manganese phthalocyanine has been used as photosensitive material for immobilization.

The BDD electrode has been electrochemically studied in three electrode cell. The electrochemical properties have been studied by Cyclic Voltammetry (CV) at different experimental conditions in dark and under illumination.

The results approve that the boron doped diamond electrode grafted with phthalocyanine serves as an efficient and stable electrode for nitrate reduction. The diamond electrode has wide potential range. The obtained results are promising for future electrochemical application.

**Keywords:** diamond electrode; electrochemistry; water treatment

### 1. INTRODUCTION

Diamond is a very hard crystalline form of carbon with unique mechanical, chemical and physical properties. Diamond as a wide bandgap semiconductor is an electrical insulator. The resistivity however can be controlled by doping mostly with boron or nitrogen [1, 2].

Today the electrochemical behaviors of boron-doped diamond films are subject of scientific and technological interest. Conducting diamond films exhibit inert surface, corrosion stability in aggressive media, wide potential window in aqueous and non-aqueous electrolytes, and low background current. Due to these properties the diamond is a very promising electrode material in various electrochemical devices [1, 3]. One of the most important advantages of the boron doped diamond as an electrode material is the high overpotential for oxygen and hydrogen evolution in aqueous electrolytes [4, 5].

The reduction of nitrates and nitrites is a very important process in the control of the wastewater. The process is kinetically unfavorable because of the highly negative redox potential of ammonia (-2.85 V vs SCE) [2, 6]. The strong cathode polarization under the conditions of ammonia production destabilizes most of the electrodes and they lose the electrocatalytic activity after several cycles. The ideal electrode material should be very stable in the

electrolyte, cheap, with high catalytic activity towards nitrate reduction and low activity towards secondary reactions [7]. Boron doped diamond meets these requirements due to its outstanding electrochemical behaviors which make it one of the candidates for application in wastewater treatment [6, 8].

The present work deals with the application of conductive boron doped diamond functionalized with phthalocyanine for the electrochemical reduction of nitrate. The phthalocyanines are organic compounds, which are thermally very stable and absorb light between 600 and 700 nm.

### 2. EXPERIMENTAL

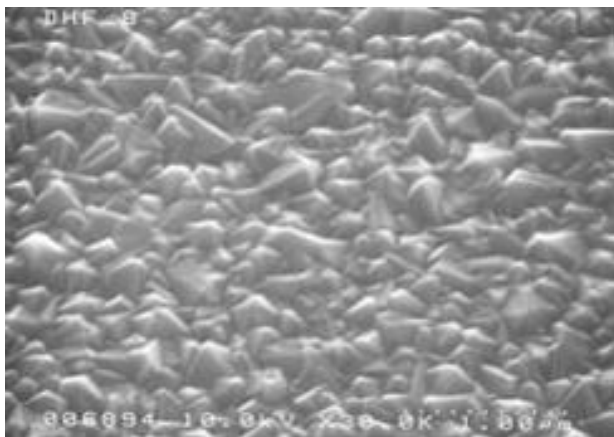
#### 2.1. Preparation of diamond films

Boron doped diamond thin films were synthesized on silicon substrate by hot-filament chemical vapor deposition (HFCVD) technique. The precursor gas was a mixture of methane and hydrogen. Typical CVD diamond synthesis includes activation of the gas mixture, gas phase reactions and a subsequent transfer of the diamond forming gas species onto the substrate surface. Scanning electron microscopy was used to reveal the homogeneous and typical morphology of the nanocrystalline diamond (NCD) films with crystallites of sub-micron size (Figure 1) [9, 10].

Boron doping was achieved by addition of trimethyl borate into the reactor chamber during the diamond growth. The NCD surfaces are chemically inert and have a hydrogen termination after the

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**Figure 1.** Top-view SEM image of NCD film.

deposition. The surface is modified by plasma- or photo-chemical processes to achieve a desired surface termination. In this work the samples were subjected to oxygen plasma modification (2.45 GHz) in oxygen asher (TePla 200-G) for 5 min at 200 W discharge power and 0.67 mbar working pressure [11]. Oxygen-terminated diamond surface shows hydrophilic character.

### 2.2. Preparation of the NCD films as electrodes

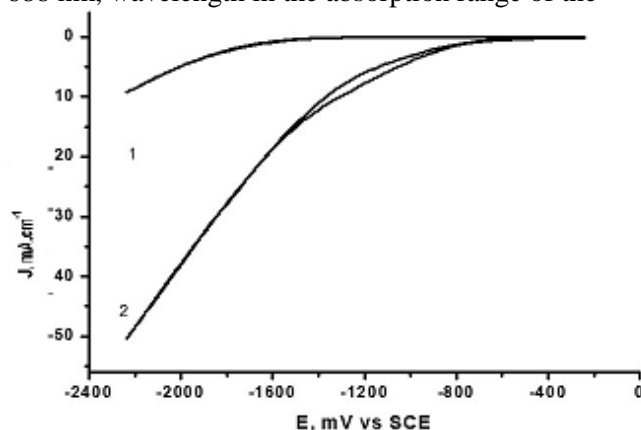
The diamond films after the modification with oxygen plasma were functionalized with a catalyst. As a catalyst in the present work manganese phthalocyanine (Mn-Pc) was used [10]. The grafting of the Pc on the NCD surface was completed as follows: the samples were immersed in Mn-Pc (1  $\mu$ M solution in  $\text{CH}_2\text{Cl}_2$ ) for 12 hours, then cleaned in ultrasonic bath with  $\text{CH}_2\text{Cl}_2$  and dried with  $\text{N}_2$  flow.

The modified with  $\text{O}_2$  plasma and functionalized with Mn-Pc films were arranged as electrodes for electrochemical measurements. The electrode was attached with silver paste to platinum wire and the assembly was tightly encapsulated in Teflon tape with a small hole. This opening was perforated before the encapsulation in order to provide a 0.5  $\text{cm}^2$  working area for the electrode.

### 2.3. Electrochemical study of the diamond electrodes

The electrochemical measurements were carried out in a three electrode cell. The boron doped diamond film was used as a working electrode with an active area of 0.5  $\text{cm}^2$ . The counter and reference electrodes were a platinum wire and a standard calomel electrode, respectively. The experimental investigations on the behavior of the conducting diamond electrode were done by cyclic voltammetry at different conditions. Experiments under illumination were carried out by

means of He-Ne laser (25-LHP-111-230) with  $\lambda=688$  nm, wavelength in the absorption range of the

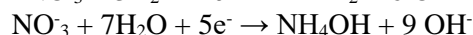
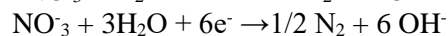
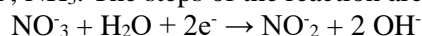


**Figure 2.** Cyclic voltammograms of a boron doped diamond in 0,1M KCl (curve 1) and 0,1M  $\text{KNO}_3$  (curve 2) at a scan rate of 50 mV/sec.

Mn-phthalocyanine. The reduction of nitrate was continuously controlled. The cyclic voltammograms were recorded in two different electrolytes – 0.1 KCl and in 0.1 M  $\text{KNO}_3$ . The reduction process was studied with Solartron with scan rates of 10 mV/sec, 20 mV/sec and 50 mV/sec. The concentration of the nitrate ions was determined titrimetrically using a modified Leithe's method [12]. The content of nitrite ions in the electrolyte was determined indirectly as a difference between titrated nitrate ions without and with added urea.

## 3. RESULTS AND DISCUSSION

One of the most suitable treatments of the nitrate containing water is the direct cathode reduction. The electrochemical reduction of the nitrate is a multistep reaction and the products expected out of these reactions are  $\text{NO}_2^-$ ,  $\text{N}_2$ ,  $\text{NH}_4\text{OH}$ ,  $\text{NH}_3$ . The steps of the reaction are:

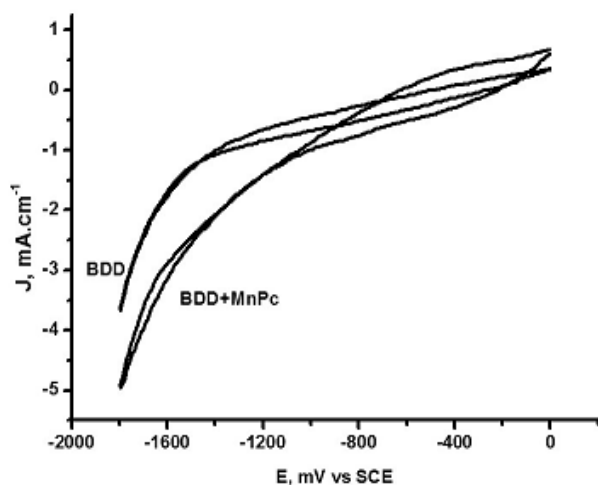


The cyclic voltammograms were achieved in 0.1 M  $\text{KNO}_3$  and 0.1 KCl electrolytes, the latter used as a supporting electrolyte (Figure 2).

The curve recorded in KCl is completely flat while on the curve obtained in 0.1 M  $\text{KNO}_3$  a slightly modified region in the potential range from -0.8 to -1.4 V is observed, most probably due to a weak reduction process. The curves approve the very large potential window of the diamond electrodes for hydrogen evolution at approximately -1.5 V in both electrolytes.

The difference in cyclic voltammograms of the boron doped diamond electrode and boron doped diamond electrode functionalized with

phthalocyanine are shown on Figure 3. The measurements are carried out in 0,1M  $\text{KNO}_3$  solution from 0 to  $-0.8$  V at a scan rate of 20 mV/sec.



**Figure 3.** Cyclic voltammograms of a boron doped diamond and boron doped diamond functionalized with phthalocyanine in 0,1M  $\text{KNO}_3$  at a scan rate of 20 mV/sec.

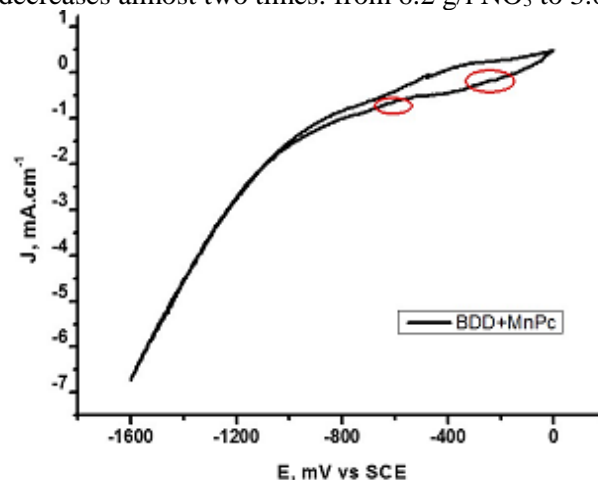
The curve recorded with the electrode with catalyst shows larger range of potentials where the reactions take place. The electrode functionalized with phthalocyanine possesses a cathode current of  $-5 \text{ J, mA.cm}^{-1}$  at  $-1,5 \text{ V}$ , while that of the boron doped diamond reaches  $-3,6 \text{ J, mA.cm}^{-1}$  at the same potential.

The reactions occurring at the electrode surface are more pronounced when a lower scan rate is applied. The curve for the electrode functionalized with phthalocyanine recorded at 10 mV/sec and under illumination is presented in Figure 4.

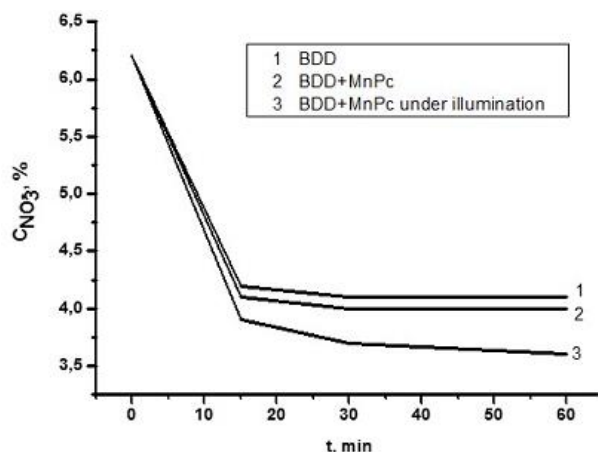
Two well visible peaks are observed at  $-0.4 \text{ V}$  and at  $-0.8 \text{ V}$  which are not present in the curves obtained at the higher scan rate. The first peak is most probably due to the reduction of nitrate to nitrite (reaction 1) and the second one can be attributed to the reduction of nitrite to ammonia (reaction 3) (Figure 4).

The experiment shows that the suitable potential for nitrate reduction as derived from the cyclic voltammetry measurements is between  $-0,4$  and  $-0,8 \text{ V}$  vs SCE. For this reason, one hour electrolysis was carried out at a constant potential of  $-0.8 \text{ V}$  in 0.1 M  $\text{KNO}_3$  electrolyte. Boron doped diamond and boron doped diamond functionalized with Mn phthalocyanine electrodes were additionally studied in dark and under illumination. The variation of the concentration of the nitrate ions measured periodically is shown in Figure 5. From the figure it can be seen that the concentration of nitrate ions is reduced in the first 15 min and

then remains constant. The most efficient reduction of nitrates is observed when the boron doped diamond functionalized with phthalocyanine was used as a working electrode under illumination. The results show that the concentration of the nitrates decreases almost two times: from  $6.2 \text{ g/l NO}_3$  to  $3.6$



**Figure 4.** Cyclic voltammogram of boron doped diamond functionalized with phthalocyanine in 0,1M  $\text{KNO}_3$  at a scan rate of 10 mV/sec under illumination.



**Figure 5.** Variation of the concentration of nitrate during one hour electrolysis in 0,1M  $\text{KNO}_3$

$\text{g/l NO}_3$  in the measurement under illumination. The nitrate concentration in the experiments with BDD and BDD+MnPc without light decreases from  $6.2 \text{ g/l}$  to  $4.1 \text{ g/l}$  and  $4.0 \text{ g/l}$  respectively (Figure 5).

The analytically measured content of the electrolyte reveals that initially, the nitrate favors the conversion to nitrite, but as the treatment proceeds and the nitrite level increases, the nitrite is further converted to either ammonium or nitrogen gas, finally disappearing by the end of the treatment.

#### 4.CONCLUSIONS

The boron doped diamond electrode grafted with phthalocyanine serves as an efficient and stable electrode for nitrate reduction. Elimination of

nitrate ions was achieved by applying an external potential to the modified and functionalized with phthalocyanine diamond electrode. The studies performed in dark and under illumination reveal that the process under light is more efficient. After 15 minutes 37% nitrate purification of the solution in dark and 42% under illumination have been achieved.

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## ДИАМАНТЕНИ ЕЛЕКТРОДИ ЗА ТРЕТИРАНЕ НА ОТПАДЪЧНИ ВОДИ

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Постъпила на 7 юли, 2015 г. коригирана на 28 октомври, 2015 г.

(Резюме)

Бор-дотирани диамантени филми (BDD) имобилизирани с фталоцианинови молекули са изследвани като материал за редукция на нитрати в отпадъчни води. Този процес е една от най-важните цели на съвременната електрохимия.

Тънките нанокристални диамантени слоеве са отложени върху силициеви подложки посредством химическо отлагане на пари (Chemical Vapor Deposition). Върху така синтезираните и опроводени слоеве за по-добра и ефективна работа, като катализатор е нанесен фталоцианин.

Получените електроди са изследвани в три електродна клетка по метода на циклична волтамперометрия. Изследванията са проведени при различни експериментални условия без и със светлина.

Получените резултати показват, че бор-дотирани диамантени електроди имобилизирани с фталоцианин могат да бъдат използвани като ефективен и стабилен електрод за редукция на нитрати. Освен това, те са обещаващ материал и за други електрохимични приложения.