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## Boron doped diamond/metal nanoparticle catalysts hybrid electrode array for the detection of pesticides in tap water

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### Abstract

Online control of the chemical composition of drinking water is one of the major challenges of our century. This issue is addressed in this work with the development of a multi-electrode array based on Boron Doped Diamond (BDD) electrodes coated with metal catalyst nanoparticles. A new physical deposition method of the nanoparticles was developed, which offers good stability in terms of electro-activity and adhesion. The sensor array was tested for the electrochemical detection of pesticides including paraoxon and imidacloprid with good discrimination between both samples. For safety reason, hydrogen peroxide was also use as an efficient redox stimulus to assess the capability of the array to operate in tap water. The detection threshold was in the order of  $19 \times 10^{-2} \mu\text{M}$  and  $33 \times 10^{-2} \mu\text{M}$  for paraoxon and imidacloprid, respectively, as measured by chronoamperometry. Chronoamperometric method demonstrated also the potential of the array to operate online directly in tap water through the detection of  $\text{H}_2\text{O}_2$ .

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*Keywords:* Boron doped diamond, metal nanoparticle, pesticides, electrochemical sensor

### 1. Introduction

BDD electrodes have been used as an innovative solution in terms of measurement speed, cost, miniaturization and sensitivity. Their introduction in electrochemical applications is due to their large panel of physico-chemical assets, such as a wide potential window in aqueous media ( $> 3\text{V}$ ), high corrosion resistance and low background current. Although such electrodes allow overcoming quite well some of the recurring problems encountered with electrochemical sensors, solutions remain to be found when it comes to chemical selectivity and the possibility to perform online measurements. These latter issues are addressed in this work with the development of a multi-electrode array based on BDD electrodes coated with metal catalyst nanoparticles (NPs). Indeed, in the last few years, several studies have led to the possibility to deposit e.g. Pt or Ir NPs onto BDD [1]. These NPs were found to exhibit some interesting electro-catalytic activity [2–4]. For instance, they have been studied for biofuel applications [1] or for sensing hazardous compounds such as pesticides in water [5]. Here metallic NPs, namely Platinum and

Iridium, were deposited by sputtering thin metal films onto BDD electrodes followed by de-wetting under hydrogen plasma. The resulting electrodes were investigated for the detection of pesticides in water. Their electrochemical detection performances were assessed by chronoamperometric method using standard solution of pesticides. Since the pesticides used are highly hazardous to human health, hydrogen peroxide was also used as an alternative redox stimulus in order to evaluate the capability of the sensor array to work online in tap water.

### Nomenclature

BDD	Boron doped diamond
NPs	Nanoparticles
Pt	Platinum
Ir	Iridium
SWV	Square wave voltammetry
CA	chronoamperometry
SEM	Scanning electron microscopy
CV	Cyclic voltammetry

## 1. Experimental

### 1.1. Chemicals

Hydrogen peroxide 35% (H<sub>2</sub>O<sub>2</sub>), LiClO<sub>4</sub>, Phosphate Buffer Saline (PBS), imidacloprid and paraoxon were purchased from Sigma-Aldrich, France. They were used without further purification. Standard solutions of pesticides for electrochemical characterizations were prepared in ultra-pure deionized water from a Millipore DirectQ3- UV with a resistivity of 18.2 MΩ.cm. The 35% H<sub>2</sub>O<sub>2</sub> solution was diluted in tap water daily as required for the online measurements without addition of any other chemicals.

### 1.2. Electrode preparation

- BDD electrode material preparation:

Boron doped diamond (BDD) was grown onto highly doped silicon substrates in a homemade microwave plasma enhanced chemical vapour deposition (MPECVD) using a process described elsewhere [6]. The film thickness was approximately 500 nm, as measured by optical interferometry, and the boron doping level was  $2 \cdot 10^{21}$  at.cm<sup>-3</sup> as determined by secondary ion mass spectrometry (SIMS) measurements. The potential window of the resulting electrodes was around 3 V in a [LiClO<sub>4</sub>] = 0.5 M aqueous solution, and their electron transfer rate 0.1cm.s<sup>-1</sup> as measured at Open Circuit Potential (OCP) by electrochemical impedance spectroscopy (EIS) using a 0.3 M KCl aqueous electrolyte containing a 10<sup>-3</sup> M equimolar solution of potassium ferricyanide (II) and potassium hexacyanoferrate (II).

- Pt and Ir nano-dots deposition onto BDD electrodes:

Pt and Ir nanoparticles were immobilized onto BDD electrodes as follows. Thin films of either Pt or Ir were deposited by physical vapour deposition onto BDD substrates at RF power 50 W and Argon chamber pressure of 6.10<sup>-3</sup> mbar, with sputtering rates of 6.63 nm.min<sup>-1</sup> for Platinum and 9.99 nm.min<sup>-1</sup> for Iridium, respectively, as determined gravimetrically. The deposition time was 7 seconds for both metals. A second step involved annealing the samples under hydrogen plasma in an AX6500X Technotron Corp diamond growth reactor, at a pressure of 40 mbar and microwave power 900 kW for 10 min in order to de-wet the metal films [7].

- Electrodes setup

Individual electrodes were mounted on glass substrates as described elsewhere [6]. Electrical contact was taken from the backside of the silicon substrate using copper tape. All conductive areas except for the active electrode surface were encapsulated in epoxy resin in order to avoid contact with the electrolyte solution.

For online measurements in tap water, an experimental set up was prepared as described in Figure 2.a. In brief, the three working electrodes including a bare BDD electrode, a BDD/Pt NPs electrode and BDD/Ir NPs electrode were fixed on one side of the flow cell, along with another BDD pseudo-reference electrode. The electrode surface area here was  $1 \text{ cm}^2$  for each electrode. The three working electrodes and reference electrode were facing a counter electrode also made of BDD, with a surface area of  $4 \times 1 \text{ cm}^2$ , placed opposite the other four electrodes as shown in Figure 2.a.

### 1.3. Electrochemical measurements

The electrochemical experiments with paraoxon and imidacloprid were performed using a palmSense EmStat3 polypotentiostat, with a five electrodes configuration (3 working, 1 reference (ref.), 1 counter (CE)) in a non-reactive, one-compartment cell. Electrochemical measurements were carried out by chronoamperometry (CA). For online measurements, the same potentiostat was used but the electrodes were fitted to the online cell as described previously and shown in Figure 2. The reference solution (tap water) or measuring solution (1 %  $\text{H}_2\text{O}_2$  in tap water) were injected in the flow cell using syringe pumps, at a flow rate of  $10 \text{ ml} \cdot \text{min}^{-1}$ .

## 2. Results

### 2.1. Imidacloprid and paraoxon detection

The deposition process allowed obtaining metallic NPs onto BDD with a narrow size distribution around typically  $10 \pm 3 \text{ nm}$ , and with a uniform size distribution across the entire BDD surface. In addition to the advantages already shown by other teams on Pt and Ir NPs, our new physical deposition method offers enhanced stability in terms of electro-activity and adhesion. This was challenged either by the repetition of up to a 100 repeat amperometric measurements or the application of 600 short current pulses of current density about  $10 \text{ mA} \cdot \text{cm}^{-2}$ , with no degradation of the electrodes. The sensor array was able to detect pesticides such as paraoxon and imidacloprid. Figure 1.a shows a typical chronoamperometric response of BDD, BDD/Pt NPs, BDD/Ir NPs, for successive additions of imidacloprid solution into continuously stirred aqueous medium. The same experiment was carried out for paraoxon with the three electrodes (data not shown). The current density response of each electrode was normalized so that the total response of all sensors was 100 % (Figure 1.c). The normalized signal intensity obtained

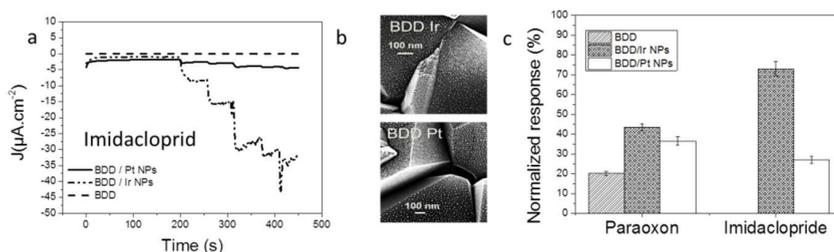


Figure 1: (a) chronoamperometric response of BDD, BDD/Pt NPs, BDD/Ir NPs, for successive additions of  $10 \mu\text{L}$  of  $5.5 \text{ mM}$  imidacloprid solution into continuously stirred aqueous medium ( $300 \text{ rpm}$ ) of  $0.3 \text{ M}$  of  $\text{LiClO}_4$  ( $\text{pH } 7.2$ ) under a potential of  $-0.8 \text{ V}/(\text{Ag}-\text{AgCl})$  with a volume of  $90 \text{ ml}$  (b) SEM characterisation of Pt and Ir NPs onto BDD. (c) The current density response of BDD, BDD/Pt NPs, BDD/Ir NPs electrodes normalized to 100 % for Imidacloprid and paraoxon.

by the three different electrodes was 0% for BDD, 27% for BDD/Pt NPs and 73% for BDD/Ir NPs, respectively. For paraoxon it was 20.1% for BDD, 36.5% for BDD/Pt NPs and 43.4% for BDD/Ir NPs. Hence, the electrode array showed a partial selectivity toward the target analytes. Indeed, when combined together, the response of the different electrodes provides to some extent a fingerprint of the detected chemical (Figure 1.c), thus suggesting that some selectivity can indeed be obtained using such a multi-sensor approach.

## 2.2. Online measurement of $H_2O_2$ in tap water

The chronoamperometric response of each electrode to 1% hydrogen peroxide in tap water is shown in Figure 2.b. Positive detection of  $H_2O_2$  is observed for both BDD/Pt NPs and BDD/Ir NPs whilst the bare BDD, as expected, did not respond, due to the low catalytic properties of the bare diamond surface. This result is a first step toward the further online measurements for hazardous molecules in tap water.

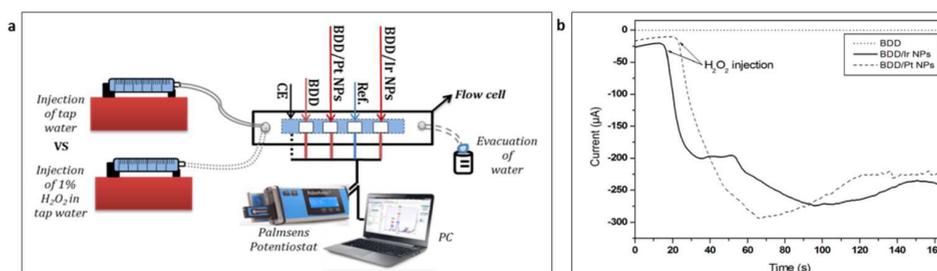


Figure 2. Experimental setup used for online detection of  $H_2O_2$  in tap water.

## 3. Conclusion

Imidacloprid and paraoxon were successfully detected using BDD electrodes decorated with Pt and Ir nanoparticles. The detection threshold was in the order of  $19 \times 10^{-2} \mu M$  and  $33 \times 10^{-2} \mu M$  for paraoxon and imidacloprid, respectively. Response time was below 15s for all electrodes at 90%. When bare BDD, BDD/Pt NPs and BDD/Ir NPs electrodes were combined into an array, some kind of discrimination was made possible between the two pesticides. The system was able to detect the presence of  $H_2O_2$  in tap water. These results are the first step toward an online and real time detection of pesticides in tap water. Hence, BDD, BDD/Pt NPs and BDD/Ir NPs can be recommended for developing a real time detector in order to control the chemical composition of drinking water.

## References

- [1] Belding, S. R., Campbell, F. W., Dickinson, E. J. F. & Compton, R. G. Nanoparticle-modified electrodes. *Phys. Chem. Chem. Phys.* 12, 11208–21 (2010).
- [2] Kitte, A., Assresahegn, D. & Soreta, R. Electrochemical determination of hydrogen peroxide at glassy carbon electrode modified with palladium nanoparticles. *J. Serbian Chem. Soc.* 78, 701–711 (2013).
- [3] Scorson, E., Saada, S., Arnault, J. C. & Bergonzo, P. Enhanced control of diamond nanoparticle seeding using a polymer matrix. *J. Appl. Phys.* 106, - (2009).
- [4] Bao, J., Dou, M., Liu, H., Wang, F., Liu, J., Li, Z. & Ji, J. Composition-dependent electrocatalytic activity of palladium-iridium binary alloy nanoparticles supported on the multiwalled carbon nanotubes for the electro-oxidation of formic acid. *ACS Appl. Mater. Interfaces* 7, 15223–9 (2015).
- [5] Rismetov, B., Ivandini, T. A., Saepudin, E. & Einaga, Y. Electrochemical detection of hydrogen peroxide at platinum-modified diamond electrodes for an application in melamine strip tests. *Diam. Relat. Mater.* 48, 88–95 (2014).
- [6] Vanhove, E., de Sanoit, J., Mailley, P., Pinault, M.-A., Jomard, F. & Bergonzo, P. High reactivity and stability of diamond electrodes: The influence of the B-doping concentration. *Phys. status solidi* 206, 2063–2069 (2009).
- [7] K. Belghiti, D., Scorson, E. & Bergonzo, P. Metal Nanoparticles/BDD Hybrid Electrodes for Analytical Detection of Pollutants in Water. *MRS Adv.* 1, 1131–1136 (2016).