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Emmanuel Scorsone, Dounia Belghiti, Massiel Habchi, P. Bergonzo. Boron doped diamond/metal nanocatalyst hybrid electrode arrays for analytical applications. ISOEN - 2017 ISOCS/IEEE International Symposium on Olfaction and Electronic Nose, May 2017, Montréal, Canada. 10.1109/ISOEN.2017.7968907 . cea-01809222

HAL Id: cea-01809222

https://cea.hal.science/cea-01809222

Submitted on 26 Jul 2023

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BORON DOPED DIAMOND/METAL NANOCATALYST HYBRID ELECTRODE ARRAYS FOR ANALYTICAL APPLICATIONS

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ABSTRACT

We report on the development of sensor arrays comprising synthetic boron doped diamond (BDD) electrodes modified with metal catalyst nanoparticles. The latter are deposited onto the BDD electrodes surface by a physical vapor deposition process followed by de-wetting under oxygen-free atmosphere in high temperature conditions. The mean size of the particles is in the order of 10 nm, as characterized by scanning electron microscopy (SEM) image processing and small-angle X-ray scattering (SAXS). The particles are made of e.g. platinum, iridium, gold, ruthenium or alloys thereof and showed good adhesion, and good electrochemical reactivity towards a wide range of redox analytes. Sensor arrays composed of 4 BDD electrodes each modified with a different nano-catalyst were mounted and tested for various analytical applications. For instance such a sensor array was able to detect online and discriminate the presence in tap water of the following contaminants: Imidacloprid, Dimethyl methylphosphonate (DMMP) or hydrogen peroxide, chosen for demonstration purpose.

Index Terms— Diamond, electrodes, nano-catalyst, sensor array, amperometric

1. INTRODUCTION

Electrochemical sensors have long been recognized as a suitable approach for the measurement of electro-active chemical species in liquid environments because of their simplicity of use, reliability, and low energy consumption. Moreover they offer good sensitivity and fast response time in compliance with the requirements of many analytical applications [1]. The measuring electrodes are often based on carbon materials or noble metals. Despite their obvious advantages for analytical measurements, they often suffer from lack of selectivity. This issue can partially be overcome either by modifying the electrode surface by ion selective membranes, specific biological receptors, etc., or by using adequate electrochemical methods such as Square Wave Voltammetry allowing the separation of species according to their direct oxidation or reduction potentials. However, the selectivity reached by these approaches is somehow limited to fairly simple analytical media and tends to fail when many interfering species are present in solution. Also they are not appropriate for the characterization of multiple analytes simultaneously in the same solution (e.g. e-tongue application for taste assessment). Furthermore, such raw or modified electrodes are often prone to fouling, which affects significantly their performances and prevent their use for online monitoring or even repeated measurements. In this context, BDD electrodes have been identified as an innovative solution for analytical measurements in particular due to their wide potential window in aqueous media (> 3V), high chemical resilience and low background current [2]. Also it was shown recently that BDD electrodes can be cleaned *in-situ* using electrochemical processes following fouling, thus opening the way to online measurements [3]. Although such electrodes allow overcoming quite well some of the recurring problems encountered with electrochemical sensors, they exhibit relatively poor surface catalytic properties, and solutions still remain to be found when it comes to chemical selectivity. These latter issues are addressed in this work with the development of a multi-electrode array based on BDD electrodes coated with metal nano-catalysts. Pt or Ir nano-particles have already been deposited in the past on BDD electrodes. These are known to bring certain properties that are not observed at the macro-scale, such as a higher surface area and enhanced diffusion that both improve catalytic activity [4]. Such electrodes were used for instance in fuel cells applications [5]. Metal nano-particles were deposited onto diamond electrodes mostly by electrodeposition [6] or ion implantation [4, 5]. Here an alternative process consisting of depositing a thin layer of metal by physical vapor deposition followed by de-wetting under oxygen-free atmosphere was used. Multi-sensor arrays combining BDD electrodes each with a different nano-catalyst deposited over its surface were mounted and tested for a range of applications ranging from foodstuff to security applications. In this paper, we focus as an example on the detection of contaminants in tap water. The multisensor array was mounted online using a dedicated flow cell and tested for the detection and discrimination of Imidacloprid, DMMP or hydrogen peroxide.

2. EXPERIMENTAL

2.1. Chemicals

Hydrogen peroxide 35 wt%, Imidacloprid and Dimethyl methylphosphonate (DMMP) were purchased from Sigma-

Aldrich, France, and used as received. Test solutions were prepared daily from tap water.

2.2. BDD electrodes preparation

BDD electrodes were grown onto highly doped <100> silicon substrates (4 inches in diameter) in a homemade microwave plasma enhanced chemical vapor deposition (MPECVD) using a process described elsewhere [3]. The film thickness measured by optical interferometry was approximately 500 nm, and the boron doping level determined by secondary ion mass spectrometry (SIMS) measurements was 2.10^{21} at.cm^{-3}. After growth the substrate was cleaved in order to get 1 cm^2 individual BDD electrodes.

2.3. Nano-catalyts deposition on BDD electrodes

Metal catalyst nano-particles of either Pt, Ir, Au, Rh were immobilized onto BDD electrodes using the following process. For each catalyst material, a thin film of metal was deposited by physical vapor deposition (RF-sputtering) onto BDD substrates at RF power 50 W and Argon chamber pressure of 6.10^{-3} mbar. The sputtering rates, determined gravimetrically, ranged from typically 5 nm.min^{-1} up to 15 nm.min^{-1} depending on the metal used. The deposition time was adjusted so that the thickness of the films were in the order of 2-3 nm. Then the samples were exposed to hydrogen plasma in an AX6500X Technotron Corp diamond growth reactor, at a microwave power 900 kW and a pressure of 40 mbar for 10 min in order to de-wet the metal films. At the end of the process small nanoparticles of metal catalysts are observed over the diamond electrode surface when observed under SEM (Fig.1). The mean particle size was assessed to be in the order 10 nm according to image processing and SAXS analysis.

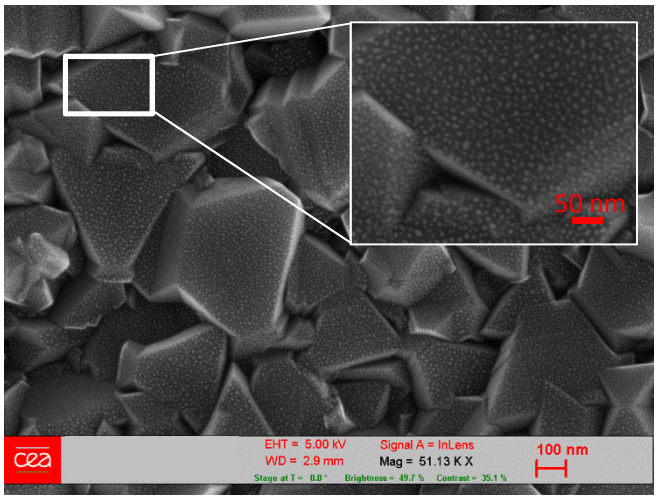

Fig.1. Example of polycrystalline BDD electrode surface modified with Iridium nano-catalyst observed under SEM imaging

2.4. Measurement setup

Four working electrodes WE (BDD, BDD-Pt, BDD-PtIr, and BDD-Ir) were mounted in a 3D printed flow cell along with a pseudo-reference electrode RE and counter electrode CE both made of unmodified BDD and positioned as shown in Fig.2. Solutions of 0.05%/wt Imidacloprid, 1%/wt Dimethyl methylphosphonate (DMMP) and 1%/wt hydrogen peroxide dissolved in tap water were prepared. The experimental setup shown in Fig.2 allowed passing tap water (V1 open, V2 closed) or contaminated tap water (V1 and V2 open) through the cell at a flow rate of approximately 300 mL.min^{-1}. Chronoamperometric measurements were performed using a Palmsense EmStat3 4WE potentiostat.

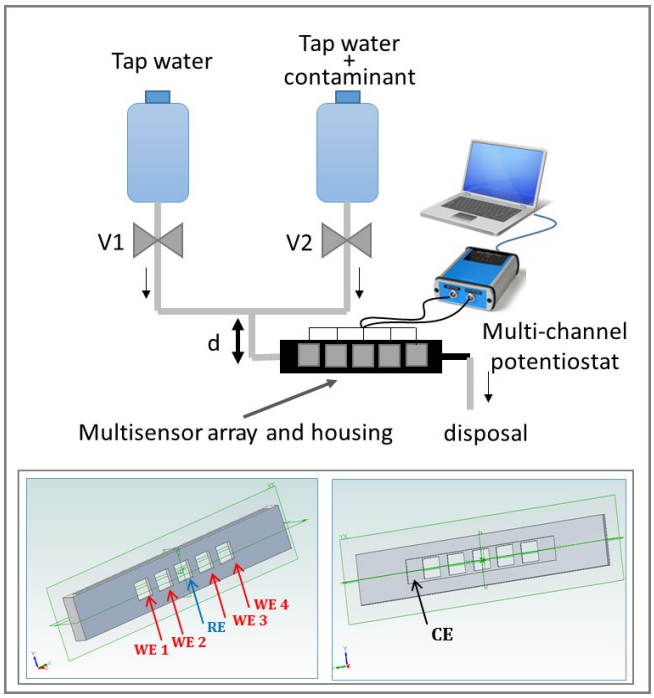

Fig.2. Experimental setup used for online measurement of contaminants in tap water using a 4-electrode multisensor array

3. RESULTS AND DISCUSSION

The sensors were exposed successively to each contaminant diluted in tap water by opening or closing valve V2 while leaving V1 always open. The distance d (see Fig. 2) was made either very short, typically less than 20 cm, or 100 m long using 3 mm external diameter PVC tubing, in the latter case to simulate water network conditions. A typical response to three exposures to 1 %/wt DMMP is shown in Fig. 3 for d= 20 cm, and a typical response to three exposures to 1 %/wt H_2O_2 for d= 100 m in Fig.4, respectively. The response signals correspond to the reduction currents of DMMP or H_2O_2 at each electrode when the electrodes are polarized at -0.1 V versus the pseudo-reference electrode. As expected, the bare BDD electrode exhibits the lowest sensitivity due to poor catalytic surface properties. However it is still of interest

within the sensor array as it may be sensitive to more reactive contaminants potentially present in tap water and thus bring some significant contribution to the overall selectivity. Both for DMMP and H_2O_2 the most sensitive electrode is by far the BDD-PtIr electrode, followed by the BDD/Ir, and BDD/Pt. This gives further evidence of the advantage of making alloy nanoparticles rather than single metal nanoparticle to enhance the catalytic reaction, as already known in catalysis chemistry. It also justifies our deposition approach since the other NP depositions approaches reported in the literature so far are to our knowledge not compatible with metal alloy NP deposition on BDD electrodes.

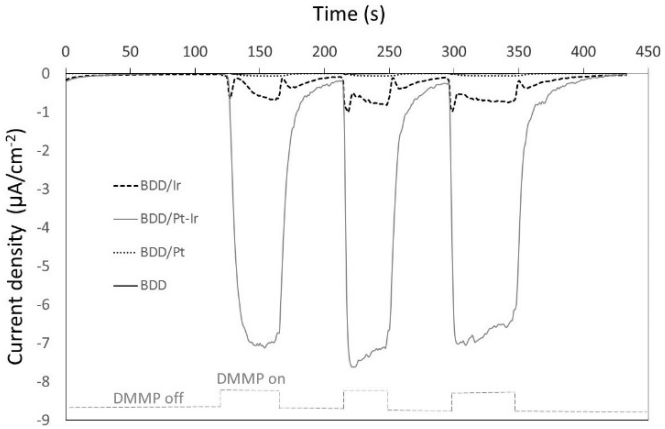

Fig.3. Typical response to three exposures to 1%wt DMMP injected in tap water close to the sensor cell

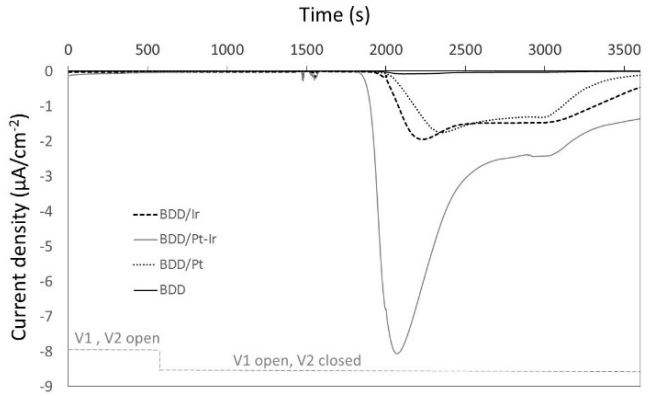

Fig.4. Typical response to exposure to 1%wt H2O2 injected in tap water 100 m away from the sensor cell location

Several exposures to Imidacloprid, H_2O_2 and DMMP were performed in the same experimental conditions for d = 20 cm by opening and closing successively V2 and the steady state electrodes response values were recorded and used for statistical analysis. A typical Principal Component Analysis (PCA) result is presented in Fig. 5 showing the classification of the three chemical and clear discrimination between the three hazardous chemicals.

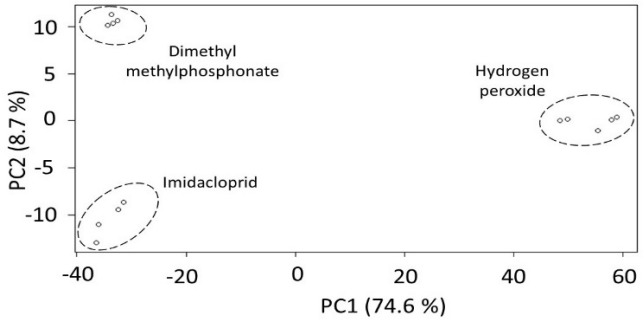

Fig. 4. PCA mapping of the three contaminants detected online in tap water using the setup shown in Fig.2, with d=20 cm.

7. CONCLUSION

A process for depositing either single metal or metal alloy nanoparticles over BDD electrodes, in order to enhance their electro-catalytic properties, has been developed and applied to the development of a multisensor array for the detection of analytes in liquid media. In this paper we demonstrated the performances of the sensor array through the detection and potential identification of contaminants in tap water. Such amperometric multisensor array would find other applications e.g. in the food industry, medical diagnostic, etc.

8. ACKNOWLEDGEMENTS

This research has been partly funded by the European Union's Seventh Framework Programme FP7/2007-2013 under grant agreement 312330.

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