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# Porous diamond with high electrochemical performance

Clément Hébert [a,*], Emmanuel Scorsone [a], Michel Mermoux [b,c], Philippe Bergonzo [a]

[a] CEA, LIST, Diamond Sensors Laboratory, F-91191 Gif-sur-Yvette, France
[b] Université Grenoble Alpes, LEPMI, F-38000 Grenoble, France
[c] CNRS, LEPMI, F-38000 Grenoble, France

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ABSTRACT

Synthetic diamond materials are currently attracting attention for applications such as thin films supercapacitors or medical implantable electrodes where chemically stable materials featuring high double layer capacitance as well as low electrochemical impedance are sought. Those properties may be reached with high aspect ratio diamond provided that current collection is done efficiently through the diamond layer. In this paper, we introduce a very novel material, namely SPDia™, based on boron-doped diamond grown on a highly porous polypyrrole scaffold prepared by chemical vapour deposition. This composite was first characterised by SEM and Raman spectroscopy to cheque the diamond crystallinity and the structural evolution of the polypyrrole during the CVD process. Then cyclic voltammetry and electrochemical impedance spectroscopy were performed to assess its electrochemical reactivity. It was found to exhibit remarkable properties, that include a large double layer capacitance with values reaching up to 3 mF $cm^{-2}$ in aqueous $LiClO_4$ and a low electrochemical impedance, thus highly competitive with respect to other nanostructured diamond materials as recently reported.



## 1. Introduction

Thin film materials exhibiting very large double layer capacitances and low electrochemical interfacial impedances are very attractive for applications such as micro-supercapacitors and neural interfacing [1–4]. Among those materials, boron-doped diamond (BDD) is promising as it features superior electrochemical properties when compared to other forms of carbon, and namely a wide electrochemical potential window in aqueous media [5] that combines with high corrosion resistance [6], chemical inertness [7], and biocompatibility [8,9]. However bulk BDD inherently exhibits both an intrinsically low double layer capacitance and a large interfacial electrochemical impedance thus limiting its attractiveness with respect to other more conventional neurointerfacting electrode materials [10,11]. These limitations can be partially solved by preparing nanostructured diamond surfaces providing, for a given electrode size, large apparent values of double layer capacitance. Several approaches to structure the diamond surface have recently been reported in the literature that can be distinguished between top down and bottom up approaches. Top down approaches mainly consist of etching the diamond electrode surface and include plasma etching [12–14], catalytic etching [15,16] or thermal etching [17]. The main advantage of these methods relies in their simplicity. However, although very promising when initially reported

* *Corresponding author.*
E-mail address: clemheb85@gmail.com (C. Hébert).
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[18], the efficiency of those processes to increase the double layer capacitance and decrease the impedance was rather limited. For example, Smirnov et al. reported on such aligned diamond vertical nanowires which exhibited only a 15-fold increase of the electrochemical double layer capacitance (EDLC) with respect to "flat" diamond, with values in the range of 70–150 μF $cm^{-2}$ [12]. In fact, it is believed that the volume conductivity of boron doped diamond is too low to ensure the top of the structures to be electrochemically active: we performed copper electroplating on such diamond nanostructures and observed that only part of its bottom structure is active.

In contrast, bottom up approaches consist of coating nanostructured highly conductive templates generally with boron-doped diamond. For example, porous films composed of silica sphere stacks exhibiting a very large double layer capacitance were reported recently [19]. However the current collection is only mediated by the sphere-to-sphere contact leading to high interface resistance. Such an issue has been overcome through the use of a highly conductive nanostructured scaffold such as multiwalled carbon nanotubes (MWCNTs) [20,21]. The low resistivity of the MWCNTs allows draining the current from the diamond surface down to the charge collection electrode with low contact resistance. Moreover the double layer capacitance of those systems can be tuned by varying the length of the CNTs [20]. Double layer capacitance values up to 1 mF $cm^{-2}$ could be obtained with such electrodes while low interfacial impedances were kept.

In the present paper we propose a novel material developed and patented at CEA Saclay and named SPDia™. Its fabrication process relies on the use of a conductive template material based on porous polypyrrole (PPy), a conductive polymer widely used in supercapacitor applications and exhibiting high porosity and high double layer capacitance [22]. The rationale for this development is to combine the very large surface area of PPy along with the outstanding surface properties of diamond in order to obtain a material exhibiting high double layer capacitance as well as low interfacial impedance, high charge storage capacitance, high resistance to corrosion and high biocompatibility. In this paper this PPy/BDD composite is at first characterised using Scanning Electron Microscopy and Raman spectroscopy. The study then focuses on the electrochemical properties of the material. The electrochemical assessment both from cyclic voltammetry and electrochemical impedance spectroscopy demonstrates that this PPy/BDD hybrid material surpasses other state-of-the-art highly porous diamond based materials, in particular in terms of capacitance values.

## 2. Materials and methods

### 2.1. Polypyrrole film preparation

Polypyrrole films were prepared using the following protocols onto 1 $cm^{-2}$ polycrystalline boron doped diamond electrodes fabricated as described elsewhere [23]. At first, a solution of 3 M $FeCl_3$ in ethylene glycol was prepared by adding gently 24.33 g of $FeCl_3$ in 50 mL ethylene glycol. 50 mL of acetonitrile was then added to the mixture, which was left to cool down to room temperature and finally stored in the dark at 4 °C overnight. Acetonitrile was then evaporated off using a Rotavapor® to obtain a viscous dark yellow solution. Next, 20 μL of this solution was deposited onto the electrodes and spread across the whole surface by spin coating. Those substrates were then exposed to saturated pyrrole (Sigma Aldrich) vapour at room temperature for 2 h. This way, pyrrole polymerises *in situ* over the sample using $FeCl_3$ as oxidising agent. The samples were then gently rinsed several times in acetonitrile until the washing solution became colourless, in order to remove the excess $FeCl_3$ and solvent. Finally the black, highly porous, PPy films featuring a film thickness of about 10 μm in thickness were dried under nitrogen flow.

### 2.2. BNCD coating over polypyrrole

The polypyrrole films were initially coated with a dense layer of diamond nanoparticles (SYP GAF 0–0.05 form Van Moppes, mean diameter 25 nm) using an electrostatic grafting process described elsewhere [24] and consisting of exposing the samples alternatively to an aqueous solution of polydiallyldimethylammonium chloride (PDDAC) and diamond nanoparticle colloidal suspension. The electrodes were then transferred into a home-made Microwave Plasma enhanced Chemical Vapour Deposition (MPCVD) reactor where the diamond seeds were grown at a temperature below 450 °C until a continuous boron doped nanocrystalline diamond layer of a few hundreds nm was obtained over the surface of the polypyrrole film. The growth parameters were 1% methane in hydrogen and 2.4% Trimethylborane (TMB) in methane. The pressure and power were set to 20 Torr and 1.2 kW, respectively.

### 2.3. Electrode characterisation

Scanning Electron Microscopy (SEM) imaging was performed using an in-lens Field Emission Scanning Electron Microscope ZEISS Supra-40, operating with an acceleration voltage of 5 kV.

Raman scattering measurements were performed using an InVia Renishaw spectrometer. It was equipped with an air-cooled CCD detector and a microscope. Two excitation wavelengths were used: the 514 nm line of an $Ar^+$ ion laser and the 785 nm line of a laser diode. A better discrimination of the different materials constituting the electrodes was obtained using the near IR excitation. Spectra were systematically acquired using a 50× (Na = 0.75) objective. The power on the sample had to be reduced down to a few tens of μW to avoid sample degradation and particularly of the polypyrrole template.

The electrochemical characterisations were performed using a Biologic SP-200 Potentiostat in a 3 electrode setup where a 0.2 $cm^2$ BDD coated polypyrrole sample is the working electrode, a Pt wire is the pseudo-reference electrode and a platinum mesh is the counter electrode. Ultrapure deionised (DI) water (Millipore Direct Q3) was used to make all the solutions. The electrochemical reactivity of the electrode was assessed in 0.1 M $LiClO_4$ solution (Sigma Aldrich) containing 1 mM potassium ferricyanide(III)/1 mM potassium hexacyanoferrate(II) trihydrate (both from Acros Organics).