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Boosting the electrochemical properties of diamond electrodes using carbon nanotube scaffolds

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ABSTRACT

Diamond is a very attractive electrode material for analytical measurements including for instance bio-sensing. However, it suffers from a relatively low double layer capacitance and high impedance when it comes to the development of supercapacitors or neural interfaces, applications for which it could also be extremely promising. One way to increase the double layer capacitance of the material is to increase its specific surface area. Here we propose here to use vertically aligned carbon nanotubes (VACNTs) with high surface areas as a template onto which boron doped diamond is grown. The resulting composite was found to exhibit a double layer capacitance as high as 0.58 mF cm^{-2} and very low impedance when compared to planar diamond electrodes in phosphate buffer saline solution. The influence of the VACNT length as well as of the thickness of the diamond coatings on the electrode performances were also investigated and are discussed in this paper.

1. Introduction

Boron doped diamond (BDD) electrodes exhibit a number of superior electrochemical properties over more conventional electrodes, such as gold or platinum, that make them highly attractive for a wide range of analytical applications. In particular, they feature a low background current resulting from an intrinsically low double layer capacitance, thus enabling high signal to noise electrochemical measurements [1]. Furthermore, their wide potential window in aqueous media, typically above 3 V, offers the possibility to detect a broad range of analytes that could not be addressed with other types of electrodes [1]. Finally, in addition to their antifouling capabilities and long term stability, Kiran et al. have demonstrated that they can be electrochemically reactivated in situ in biological fluids thus opening the way to continuous monitoring [2]. Due to the combination of those exceptional properties, BDD based electrochemical sensors have been reported e.g. for the detection of glucose [3], catecholamine [4], norepinephrine [5] etc.

More recently, BDD electrodes have also been identified as a promising material for implantable stimulation electrodes [6]. Such electrodes are used to generate an electric field gradient that produces a compensating flux of charges toward the neurons and tissues surrounding the electrode, which is high enough to fire neurons. In this context, several studies have indicated that diamond is both biocompatible [7–8] and chemically inert, which are two prerequisites for

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long-term tissue implantation. Nevertheless, even though the electrode must be capable of injecting enough charges to fire neurons for decades without degradation of the material, it must also not exceed voltage limits where the pH would evolve thus resulting in tissue degradation. Here the wide potential window of diamond is seen as a significant asset to enable injection of sufficient charge while remaining within the water electrolysis limits.

Nevertheless, in contrast with electrochemical sensors where faradic currents are mostly involved, for implantable device applications BDD electrodes suffer in this case from a low double layer capacitance and a high impedance compared to the leading materials in those applications, which limit the amount of injectable charges [9]. One approach to increase the double layer capacitance of the electrode is to change the intrinsic properties of the bulk material. This was investigated by Garrett et al. who reported on the use of nitrogen doped ultra-nanocrystalline diamond. By using an appropriate activation treatment, they were able to achieve safe charge injection capacity up to 163 μF cm^{-2}. An alternative approach is to structure the diamond in order to increase it specific surface area. Several strategies have already been explored including the formation of diamond wires by dry etching [10], diamond foam [11] or porous diamond surfaces [12,13]. Nevertheless, although those structures seem to be successful in increasing the electrochemical capacitance of the electrodes, unfortunately the impedance remains relatively high. In the current work, we study the use of diamond coated carbon nanotube bundles as a new electrode material combining low impedance, high capacitance, high stability and fairly wide potential window in water. Carbon nanotubes (CNTs) actually offer a large surface area and a high electrical conductivity to collect large currents, resulting in low interface impedances and large double layer capacitances. However they suffer from a lack of stability because of delamination and of small potential window. These issues may be overcome by strongly bonding the CNTs to the diamond substrate [14] and coating them with diamond. Such composite materials was already reported [15–17] but not investigated in terms of electrochemical properties. Here the material was characterized by cyclic voltammetry and electrochemical impedance spectroscopy according to the carbon nanotube length and the diamond coating thickness. Such electrode material is promising for many applications including for instance chemical/biosensors, where the increased surface may offer a larger number of active sites thus a better sensitivity, as well as for implantable electrodes and water based supercapacitors.

2. Experimental

A 4 inches silicon wafer was initially seeded with detonation diamond particles (ND-H_2O-5 from Adamas Nanotechnologies) using a process described elsewhere [18], in order to obtain a particle density of approximately 10^{11} cm^{-2} over the wafer. The wafer was then placed into a commercial Micro Wave Plasma enhanced Chemical Vapor Deposition (MPCVD) reactor (Seki Technotron AX6500X) where a 1 μm thick conductive diamond film was grown, using growth parameters reported elsewhere [19]. Next, a 7 nm nickel layer was deposited onto the diamond surface by e-beam evaporation. The nickel film was turned into nickel nanoparticles of approximately 50 nm by dewetting at 700 °C for 3 min. The particle density was higher than 10^9 cm^{-2}. These particles were used as catalyst for the growth of vertically-aligned carbon nanotubes (VACNTs) in a PECVD "Black Magic" AIXTRON reactor. The VACNT growth parameters are given in Table 1. Very dense VACNTs with an average diameter of 50 nm were obtained with lengths varying from 1 to 3 μm depending on the growth duration.

Table 1 – Growth parameters for the CNT growth.

Substrate temperature	750 °C
Gas mixture	NH3 (185 sccm):C2H2 (65 sccm)
Pressure	6 mBar
Plasma power	75 W

After growth, the resulting VACNTs are hydrophobic. Therefore, in order to ease seeding, they were made hydrophilic by exposure to an ozone atmosphere for typically 2 h. Then they were coated with a dense layer of 25 nm diamond nanoparticles (SYP GAF 0-0.05 form Van Moppes) using a layer-by-layer deposition process described elsewhere [20] consisting of exposing the substrate successively to solutions of polydiallyldimethylammonium chloride (PDDAC) and diamond nanoparticles. Next the diamond seeds were grown at fairly low temperature (typically 500 °C) in a home-made MPCVD reactor until a thin BDD film was obtained at the surface of the VACNTs. The growth parameters here were 1% methane and 12% TMB in hydrogen, and the pressure and power were set to 20 Torrs/20 W. The growth durations were set to 3, 20 and 40 h leading to a diamond coating of typically 30, 200 and 400 nm, respectively.

The BDD coated carbon nanotubes were characterized by Scanning Electron Microscopy imaging (SEM) using an in-lens Field Emission Scanning Electron Microscope ZEISS Supra-40, operating with an acceleration voltage of 5 kV. Cyclic voltammetry and impedance spectroscopy were performed using an Autolab PGSTAT 302 potentiostat. EIS was recorded over a frequency range of 50 kHz–0.1 Hz with logarithmic point spacing and potential amplitude of 0.01 V rms, while the working electrode was maintained at open circuit potential. Electrochemical characterizations were carried out either in Phosphate Buffer Saline solutions to evaluated the performance of the electrode in a biological-like medium, or in an aqueous solution containing 0.5 M potassium chloride (Acros Organics), 1 mM potassium ferricyanide(III) and 1 mM potassium hexacyanoferrate(II) trihydrate (both from Acros Organics) in order to characterize the electrochemical reactivity of the electrode. The counter electrode was a platinum wire and an Ag/AgCl electrode was used as the reference throughout. Raman measurements were performed using an InVia Renishaw already described elsewhere [21].

3. Result and discussions

The VACNT forests were observed under SEM imaging after seeding with diamond nanoparticles, which confirmed