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Electrochemical characterization of porous boron-doped diamond prepared using SiO_2 fiber template

Z. Vlčková Živcová[a,*], V. Mortet[b,c], A. Taylor[b], A. Zukal[a], O. Frank[a], L. Kavan[a]

[a] J. Heyrovsky Institute of Physical Chemistry of the AS CR, v. v. i., Dolejškova 3, 182 23 Prague 8, Czech Republic
[b] Institute of Physics of the AS CR, v. v. i., Na Slovance 2, 182 21 Prague 8, Czech Republic
[c] Czech Technical University in Prague, Faculty of Biomedical Engineering, Sítná 3105, 272 01 Kladno, Czech Republic

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ABSTRACT

Porous boron-doped diamond (BDD) is fabricated by consecutive plasma enhanced chemical vapor deposition on a 3D porous SiO_2 fiber template deposited by spin coating (SC). The fabricated highly doped and mechanically stable porous BDD layers are characterized by scanning electron microscopy (SEM) and Raman spectroscopy. The roughness factor of the prepared porous BDD, depending on the number of porous layers, was determined from cyclic voltammetry (RF_{CV}) and from krypton adsorption isotherms – BET, (RF_{BET}). Differences in determination of the roughness factor using these two methods are discussed. Electrochemical measurements (cyclic voltammetry and galvanostatic charge/discharge cycling) of porous BDD are performed in aqueous electrolyte solutions with different composition and pH values. The highest electric double-layer capacitance of ca. 2 mF·cm^{-2}, related to the projected geometric (2D) surface area, is obtained for the thickest (26 μm) porous BDD electrode measured in 0.5 M H_2SO_4 electrolyte solution. The capacitance of the same porous BDD normalized to the total physical surface area (3D) determined by BET is 45 μF·cm^{-2}. The electrocatalytic activity of porous BDD electrodes is studied using a hexaammineruthenium(III/II) redox probe, and the electrochemical cycle stability is determined by galvanostatic charge/discharge. The charge retention of the thickest porous BDD samples after removal of non-diamond impurities by an oxidative treatment is ca. 77% after 3000 cycles.

1. Introduction

Controlled enlargement of the specific surface area of an electrode is required for electrochemical applications, such as electroanalysis [1–5], neural interfacing [6], dye-sensitized solar cell (for increasing the number of attached dye molecules and hence the efficiency) [7–11], or energy storage in electrochemical supercapacitors [12–17]. In comparison with other carbon materials commonly used for the preparation of nanostructured porous electrodes, boron-doped diamond (BDD) offers several advantages such as superior hardness [18], high thermal conductivity [18], chemical and physical stability [19], optical transparency [20], electrical properties tunable by doping level [21], wide electrochemical potential window in aqueous media [22], as well as various functionalization routes available for the attachment of different molecules, for example DNA [23] or photosensitive dyes [7–11]. Electrochemical double-layer capacitance and its electrochemical stability after long term galvanostatic cycling are very important characteristics specifically in the case of using porous BDD as a capacitive electrode for supercapacitor devices. These properties not only depend on the quality of the BDD, e.g. the non-diamond carbon content (increasing sp^2 content increases the electrochemical capacitance), but also on the electrode nanostructuring preparation method, the shape, size and pore size distribution [17]. Various nanostructuring methods have been studied; mask assisted etching [24–26], mask-less etching [27] and deposition on a porous template [28–33]. The first reports of BDD deposition on porous templates have demonstrated the potential of these methods for fabrication of porous BDD electrodes for electrochemical applications. BDD grown on a SiO_2 fiber template by plasma enhanced chemical vapor deposition (PECVD) has been reported by other groups, e.g. Kondo et al. [28], Ruffinatto et al. [29] or Singh et al. [34]. Kondo et al. prepared BDD hollow fiber membrane (BDD–HFM) using a quartz filter substrate, which was subsequently removed by etching in HF/HNO_3 aqueous solution. This BDD–HFM electrode exhibited a double-layer capacitance per unit weight, determined from cyclic voltammetry measurements, up to ca. 13 F·g^{-1} in an aqueous electrolyte solution [28]. Preparation of BDD porous membranes (BDD-PMs) using a fiberglass filter substrate was described by Ruffinatto et al. [29], but detailed information about specific surface area and double-layer capacitance was not reported. Gao et al. [30] successfully prepared porous BDD in several layers (diamond foam) by coating silica

* Corresponding author.
E-mail address: zuzana.vlckova@jh-inst.cas.cz (Z. Vlčková Živcová).

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spheres and obtained a capacitance of 0.598 mF·cm^{-2} in aqueous electrolyte solution, and 0.436 mF·cm^{-2} in aprotic media. The specific surface area in this case was further increased upon the removal of the silica template by hydrofluoric acid. Hébert et al. [35] prepared a material (SPDia™) based on boron-doped diamond grown on a highly porous polypyrrole scaffold exhibiting double layer capacitance of 3 mF·cm^{-2} in aqueous $LiClO_4$ solution. BDD deposition on dense arrays of vertically aligned carbon nanotubes has been demonstrated to increase surface areas [36,37]. The reported method leads to an increase in specific surface area by two orders of magnitude and gave a capacitance value of 0.58 mF·cm^{-2} [36]. However, for all of these methods, the penetration of atomic species and molecular radicals necessary for diamond growth (e.g. H˙, CH_3˙) in a 3D porous template are intrinsically limited in conventional PECVD reactors, which results in a high sp^2 content deep inside the porous layers. Hence, diamond deposition on SiO_2 filter substrate relies on the large porosity of the 3D template and low self-masking effect, which minimizes sp^2 formation in 3D templates (cf. Kondo and Ruffinatto works) [28,29]. These reports also lack the necessary detailed structural and electrochemical analysis to access the full potential of fabricated materials.

In our previous work, we circumvent this intrinsic limitation using a new multi-step method based on diamond coating on a thin SiO_2 fiber template prepared by spin-coating [38]. In contrary to previous studies, consecutive deposition on thin porous templates results in a compact and homogeneous porous BDD layer without thickness limitation, leading to the possibility of fabrication of freestanding porous BDD plates [39]. In this work, we have focused on further structural and detailed electrochemical study of porous BDD electrodes prepared by this new method for their prospective electrochemical applications. Layers with various numbers of consecutive diamond coatings have been characterized by scanning electron microscopy, Raman spectroscopy, krypton adsorption isotherms (BET; to measure the surface area enlargement) and by galvanostatic charge/discharge and cyclic voltammetry in different electrolyte solutions.

2. Experimental

2.1. Sample preparation

Porous BDD layers have been deposited on silicon substrates, which had a flat BDD base layer. Microwave plasma enhanced chemical vapor deposition (MW-PECVD) used an ASTeX 5010 reactor from Seki Technotron (Japan) under the following deposition conditions: 1% of methane in hydrogen, gas pressure equal to 50 mbar, a microwave power of 1250 W and a substrate temperature of c.a. 720 °C. Boron-doping was carried out by the addition of trimethylboron in the gas phase as a boron precursor at a B/C ratio of 2000 ppm. Silicon substrates were initially ultrasonically cleaned in acetone and ethanol, and seeded using a diluted nanodiamond particle aqueous colloid (NanoAmando) from NanoCarbon Institute (Japan) for the deposition of a thin (ca. 250 nm) flat BDD base layer before the deposition of the 3D porous template. Thick porous BDD layers were obtained by multi-step diamond deposition on a porous template. The latter was deposited by spin-coating (at 3000 rpm for 30s). The porous template consists of a mixture of a polymer, a positive tone photoresist (ma-1210 from Microresist Technology), and electrospun SiO_2 fibers with typical diameters of several hundreds of nm from Elmarco Ltd. (Czech Republic). The purpose of the polymer is to homogenize and stabilize the 3D template of SiO_2 fibers before the microwave plasma enhanced chemical vapor deposition. Prior to mixing with the polymer, fibers were ultrasonically chopped in deionized water for 10 min using a UP400S Ultrasonic processor, dried, seeded with the nano-diamond particle aqueous colloid described above, and finally dried. Fibers were ultrasonically mixed with the polymer with a final concentration of 100 mg/ml. After spin coating of the fiber-photoresist mixture on the Si substrate, samples were baked at 110 °C for 90 s on a hot plate. During the diamond deposition, the photoresist was decomposed and the SiO_2 fibers were coated with BDD. The deposition of the template precursor and the diamond coating were repeated several times to increase the porous BDD thickness. The surface of the flat BDD substrate and porous BDD layers was hydrogen terminated (as-grown). Additionally, for comparison, the thickest as-grown porous BDD sample (6 layers) was treated in an oxidizing mixture of hot concentrated H_2SO_4 and KNO_3 solution to remove co-deposited sp^2 carbon impurities and finally re-terminated with hydrogen in a H plasma.

2.2. Structural and electrochemical characterization

The morphology and quality of the fabricated porous BDD layers were evaluated by scanning electron microscopy (FERA 3, TESCAN, Czech Republic) and by Raman spectroscopy (Renishaw inVia Raman microscope using a 50× Olympus objective, 488 nm excitation wavelength, laser power of 2.6 mW). The surface area of porous BDD samples was determined by krypton adsorption isotherms (BET) at 77 K (ASAP 2020 apparatus, Micromeritics, USA). The total physical surface area of the studied samples was obtained after subtracting the contribution of the empty cell. A blank experiment confirmed that the Kr adsorption capacity of a clean Si-substrate was negligible, i.e. an empty cell and a cell with a pristine Si-substrate provided identical values within the experimental error of the measurement. All measured samples (with and without porous BDD films) had a nearly identical size and shape. X-ray photoelectron spectra (XPS) were recorded using an Omicron Nanotechnology instrument equipped with a monochromatized AlKα source (1486.7 eV) and a hemispherical analyzer operating in constant energy mode with a multichannel detector. The CasaXPS program was used for spectra analysis.

All electrochemical measurements (cyclic voltammetry – CV and galvanostatic charge/discharge cycling) were performed in aqueous electrolyte solutions; (i) phosphate buffer solution with pH 7.00 (PBS, Sigma Aldrich) and (ii) 0.5 M H_2SO_4 with pH 0.8, using a three-electrode cell. Flat or porous BDD films served as a working electrode, a platinum mesh as a counter electrode and Ag/AgCl electrode (sat. KCl) as a reference. Electrochemical experiments were carried out using an AUTOLAB PGSTAT128N potentiostat (Metrohm) controlled by GPES4 software. For the electrochemical kinetic measurements solution of 10 mM hexaammineruthenium(III) chloride ($[Ru(NH_3)_6]Cl_3$, Sigma Aldrich, 98%) in 0.1 M KCl (Sigma Aldrich, ≥99%) supporting electrolyte was employed. Electrochemical measurements were carried out in a closed cell under argon atmosphere.

3. Results

3.1. Structural characterization – SEM and Raman spectroscopy

Fig. 1 displays scanning electron microscopy images of pin-hole free and well facetted flat 250 nm thick BDD coated silicon substrates (top left) and the porous BDD layers for a rising number of consecutive spin-coating steps (1st step – top right, 2nd step – bottom left, and 6th step – bottom right; for the 3rd, 4th and 5th steps see Fig. S1). The 3D template is homogenously coated by polycrystalline diamond. The diamond coating interlocks and stabilizes the SiO_2 fiber template and anchors it to the diamond coated substrate as shown in Fig. 1. The porous layers are all homogeneous except for the first one (top right) due to an irregular distribution of the fibers on the flat BDD substrate during spin-coating. The thickness of the porous layer steadily increases, at a rate of ca. 4.4 μm/step, with the number of coating steps. The final porous BDD film after 6 consecutive spin-coating deposition steps has a thickness of c.a. 26 μm. Its total physical surface area was measured by Kr adsorption (BET) and expressed as the roughness factor (RF_{BET}). The latter is defined as a ratio between the total physical surface area and the projected cross-sectional geometric area. For the abovementioned 6-layers film (26 μm thick) we found $RF_{BET} \approx 44$ (Table S1), and a density of ca.