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Diamond porous membranes: A material toward analytical chemistry

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ABSTRACT

In this study, novel diamond porous membranes are developed through a reliable process providing a unique pathway toward large surface area and porous materials. Mainly deposited onto flat surface so far, we demonstrate here that diamond coating is possible on very complex 3D shapes, even nanoporous ones, through an original nanoseeding process and adapted growth conditions. Such membranes or filters exhibit outstanding features thanks to the unique mechanical properties and surface chemistry of diamond. Indeed, the straightforward tuning of their surface properties associated to their high stability ensures the diamond porous membranes' applications in the scope of filtration, separation and extraction. Preliminary electrochemical studies highlight the membranes' potential to be used for high specific area electrode applications. After an extensive characterization of these new diamond porous membranes, their potential for protein extraction will be demonstrated through mass spectrometry detection.

1. Introduction

Conventional analytical techniques require sample preparation steps [1] where several different approaches have been used to increase the specificity, the sensitivity and the accuracy of analytical detection tools. Among the current methods, solid phase extraction (SPE) [2,3] stands out as the most suitable technique due to its low cost, its efficiency and its simplicity. SPE is mostly used for trace element detection [4] and analyte isolation in complex matrices [5]. Regarding industrial or large-scale applications, such as drug detection in biological fluids, pollutant trace detection and pharmaceutical and biological analyses, SPE remains the common technique used for sample preparation. One can note that the solid phase microextraction (SPME) approach is a faster and simplest derivative technique. Despite a lower retention potential when compared to conventional SPE, SPME is particularly well-adapted for field and on-site applications [6–8]. For an efficient SPE, the solid phase has to meet (i) a high surface area (ii) the best pore size homogeneity and (iii) an adapted surface chemistry. Up to now, silica solid phase remains the main material available on the marketplace due to its low cost and the large choice of bead size. However, the use of such silica phase involves complicated surface functionalization steps where glovebox conditions are often required. Indeed, although easier techniques such as silanization are available, the functionalized layers obtained are rather unstable thus not reliable.

In this context, we propose here a new approach where diamond can be used as an active solid phase material exhibiting very versatile and robust functionalization properties. Diamond exhibits many singular physical and chemical properties that drew the attention of numerous research groups with many and varied activities [9]. Its highest hardness associated to tremendous resilience gives diamond outstanding mechanical properties. Furthermore the high bonding energy of sp^3 carbon bonds offers several unique features. For instance, diamond exhibits high working temperatures, total inertia toward ionization radiations and a chemical inertness. In terms of surface chemistry, diamond benefits from the usual carbon chemistry. Many functionalization routes are available not only in organic but also in aqueous phases. It provides access to the grafting of a wide range of cheap chemicals and so to numerous terminal moieties. Moreover, several functionalization ways lead to the formation of highly stable C–C covalent bonds. At last, diamond can be grown at a low cost to be either a highly insulating material or a conductive medium when doped with boron. Heavily boron doped diamond gives rise to an electrode material with a very large potential window in water and a low background current. The association of these two singular properties ensures diamond electrodes' unique perspectives in terms of detection, water treatment and depollution processes in water [10]. Besides its intrinsic antifouling capabilities [11], unusual defouling processes have also been made available [12], that allows a complete regeneration of the diamond electrode surfaces. This opens up the field for the detection of a large amount of species involving a fast, complete and irreversible fouling of usual electrodes through surface polymerization [16]. It also allows detection in media with high fouling capabilities, such as milk, blood and mud, without the need of electrode replacement or abrasion.

Following this unique combination of mechanical properties, chemical inertness and anti-fouling solutions, boron doped diamond porous membranes (BDD-PMs) appear as a very promising material for high flow microfiltration, and especially when made compatible with many

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industrial filtrations such as beverage and food processing and wastewater and water treatment. One can note that several studies have already highlighted the interest of diamond to be used as a platform for separation science [13], as a highly stable phase for SPE [14] and more generally as adsorbents for applications in chromatography [15]. Moreover, the variety, simplicity and stability of the grafting techniques onto diamond make BDD-PM a valuable candidate for solid phase extraction.

Surprisingly, there are very few studies available in the literature focusing on diamond material applications for SPE and they are all related to diamond nanoparticles [17,18].

Conventional chemical vapor deposition (CVD) appears as one of the techniques available for diamond layer synthesis. To achieve porous materials, two approaches can be considered: (i) the first being based on etching processes [19,20] and (ii) the second consisting in diamond coating of already porous substrates. This latter method has already been experienced in the literature, at least on carbon nanotubes [21,22], and appeared to us as the most valuable technique. Here, we propose a coating method based on an optimized nano-seeding process via a layer by layer approach [23].

In this communication, we will detail how we have optimized this seeding approach to allow effective 3D diamond coating in order to fabricate a new type of boron doped diamond porous membrane (BDD-PM). The substrates used were low cost commercial fiberglass filters. A complete characterization that involves crystalline, chemical characterization as well as pore size assessment was carried out. A preliminary approach of the electrochemical assets of the membranes is introduced. Then, the BDD-PM extraction properties will be assessed through the filtration and extraction of the BSA followed by its detection with liquid chromatography tandem mass spectrometry (LC–MS/MS).

2. Experimental

2.1. Chemicals

Lithium perchlorate, potassium ferricyanide, potassium ferrocyanide, phosphate buffered saline, sodium phosphate dibasic, and sodium hydroxide were purchased from Aldrich.

2.2. Seeding through Buchner filtration process

HPHT (high pressure high temperature) diamond nanoparticles (NDs) were purchased from Van Moppes (Syndia SYP 0-0.02). They exhibit an average size of 30 nm and a zeta potential value of around −50 mV. Poly(diallyldimethylammonium chloride) (PDDAC, molecular weight 100,000–200,000) was purchased from Aldrich. 25 mm Whatman glass microfiber filters Grade GF/F and GF/B were purchased from Aldrich.

The filtration process was carried out through a Buchner funnel connected to a primary pump. The flow rate was tuned thanks to a vacuum manual valve. The seeding speed has been set around 1 ml/min. In the first step, 20 ml of a solution of PDDAC 1% is directly filtered on the commercial fiberglass 'as received'. Then, the filter is rinsed with UPW and 30 ml of a 0.005% (w/w) solution of NDs with a 30 nm mean diameter is filtered. In the end, the filter is rinsed with UPW and dried.

2.3. Diamond growth

Diamond depositions were prepared through microwave plasma enhanced chemical vapor deposition (MPCVD) technique using a homemade cylindrical shape metal reactor. Growth conditions with pressure and power of 10 mbar and 550 W, respectively, were used to reach a temperature on the substrate holder of 500 °C. The precursor gas mixture consists of hydrogen, methane and trimethylboron (TMB) at flow rates of 100, 1 and 12 sccm, respectively.

2.4. Polystyrene (PS) beads and pore size measurements

Solutions of fluorescent Latex beads of 2, 1, 0.5 and 0.1 μm in diameter were purchased from Aldrich. 5 ml of each PS bead size solution was filtered through the diamond membranes to measure their porosity. After this step, 5 ml of toluene is filtered through the membranes that are left soaking for 12 h in order to dissolve any PS beads remaining. Then, the filter is thoroughly rinsed with isopropanol and finally with water.

2.5. Photochemical oxidation of diamond

The membrane was oxidized through a photochemical treatment under oxygen in order to confer to the material as a hydrophilic character. During this process, low pressure oxygen (400 mbar) is exposed to UV light using a xenon excimer lamp (172 nm). This step involves oxygen radicals and ozone active species that react with the diamond surface. It has been shown that this surface treatment leads to hydroxyls and ethers' surface moieties [24]. Before oxidation, the hydrophobic character of the hydrogenated diamond membrane is illustrated through the water droplet angle depicted in the Supporting information. After oxidation, the high hydrophilic character of the membrane does not allow water droplet formation anymore.

2.6. XPS and Raman characterization

Diamond surfaces were analyzed by high resolution X-ray photoelectron spectroscopy (XPS). As X-ray source, a monochromatized Al $K\alpha$ anode (1486.6 eV) was used calibrated versus the Au $4f_{7/2}$ peak located at 84.0 eV. The spectrometer was equipped with an EA 125 hemispherical analyzer. The pass energy was 20 eV, corresponding to an energy absolute resolution of 0.6 eV. Measurements were done at 51° detection angle. The XPS data of the C1s spectral region were corrected thanks to a Shirley-background subtraction. To obtain the peak positions and relative contributions of chemically shifted components, a fitting procedure was applied using Voigt functions. Raman analyses were carried out with a LAbRAM HR Jobin Yvon. A 514 nm excitation wavelength associated to a confocal aperture of 100 μm and 120 s of acquisition time were used.

2.7. Diamond membrane functionalization

A functionalization technique based on the spontaneous and direct grafting of aliphatic amines onto hydrogenated diamond was used. This grafting method was previously proposed [25,26] and can be compared with a nucleophilic substitution where the ammonium moiety acts as a leaving group. The grafting solution is made of 10 mM of butylamine in an aqueous solution containing 0.2 M of phosphate monobasic adjusted at pH 10. First, 2 ml is filtered in order to wet the membrane, this latter is then dropped into 5 ml of the grafting solution for 12 h. Finally, the membrane is thoroughly rinsed with water and dried.

2.8. LC tandem mass spectrometry

Enzymatically digested samples were diluted in 0.1% formic acid (1:5, v/v) and analyzed by LC–MS/MS. LC–MS/MS experiments were performed on a Dionex U3000 LC system coupled to a qExactive mass spectrometer, both from Thermo Scientific (San Jose, CA, USA). Chromatographic separation was performed on a Zorbax SB-C18 column (150 × 2.1 mm i.d., 5 μm particle size, 300 Å porosity) from Agilent Technology (Palo Alto, CA, USA). Peptides from BSA were eluted from the column at a flow rate of 200 μl/min using water as mobile phase A and acetonitrile as mobile phase B, both containing 0.1% formic acid. A fast linear gradient from 5 to 60% B in 8 min was performed. Then the column was washed for 2 min at 95% B. The equilibration time before