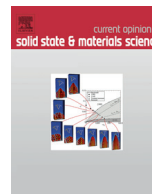




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Hydrogenated nanodiamonds: Synthesis and surface properties

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ABSTRACT

The present paper provides first a state of art on hydrogenation treatments performed either by plasma or by annealing. To compare with other surface terminations, specific assets of hydrogenated diamond surface for grafting are detailed and the different grafting routes achievable on hydrogenated nanodiamonds are summarized. In the last part, their reactivity with water molecules as well as their colloidal properties are presented and it will be shown that it is possible to render hydrogenated nanodiamonds active for radiosensitization applications.

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1. Introduction

Diamond nanoparticles or nanodiamonds are currently used or developed for many areas of applications, including medical field (for both diagnostic and therapy), composites materials [1] or even for lubricants [2]. These developments are rendered possible because of their versatile surface chemistry, previously demonstrated on diamond surfaces, improving the interactions between the particle and its environment. To start with functionalization, numerous efforts have been done to get first homogeneous surface terminations [3]. Among the investigated surface modifications, hydrogenation can combine the removal of non-diamond carbon, the elimination of oxygen groups and the stabilization of C–H terminations at nanodiamond surface. Moreover, the hydrogenated diamond surface behaves specific surface properties like its negative electron affinity (NEA) which could be exploited.

The present paper provides first a state of art on hydrogenation treatments performed either by plasma or by annealing. To compare with other surface terminations, specific assets of hydrogenated diamond surface for grafting are detailed and the different grafting routes achievable on hydrogenated nanodiamonds are summarized. In the last part, their reactivity with water molecules as well as their colloidal properties are presented and it will be shown that it is possible to render hydrogenated nanodiamonds active for radiosensitization applications. From our knowledge, this later application is the first evidence that hydrogenated nanodiamonds could be used not only as passive

cationic carriers but also as active nanoparticles for bioapplications. Based on current known properties of hydrogenated nanodiamonds, remaining challenges dealing with material, colloidal properties and interactions with water are discussed.

2. Different strategies for hydrogenation

In the literature, different methods were developed to efficiently hydrogenate the surface of nanodiamonds. The starting point is linked to the high reactivity of atomic hydrogen towards carbon species. Commonly used to clean diamond substrates before Chemical Vapor Deposition (CVD) growth [4], atomic hydrogen induces an efficient etching of non-diamond carbon (a-C or sp²-C), a removal of oxygenated groups and the formation of C–H bonds at the diamond surface. The efficiency of atomic hydrogen produced by tungsten hot filament to react with nanodiamonds was first evidenced by X-ray Photoemission Spectroscopy (XPS) [5]. After hydrogen exposure, the graphitic species initially present on nanodiamonds were removed. Moreover, a band bending was observed for hydrogen treated nanodiamonds. The later result suggests the formation of C–H bonds at nanodiamond surface.

Two main approaches are currently used to modify nanodiamonds, either by exposure to hydrogen CVD plasma or by annealing under hydrogen flow.

2.1. Plasma assisted hydrogenation

Yeap et al. reported first the use of a microwave plasma CVD (MPCVD) for hydrogenation. A double MPCVD exposure of

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60 min with a microwave power of 800 W was applied to oxidized detonation ND. C–H and OH groups were detected by Fourier Transform Infrared Spectroscopy (FTIR) on hydrogenated ND [6]. The presence of OH bonds could be linked either to an incomplete hydrogenation or to the high reactivity of ND–H towards water molecules. This second aspect will be later discussed (Part 4). Then, Girard et al. developed a home-made set-up which allows the exposure of 100 mg of nanodiamonds to a hydrogen MPCVD plasma (Fig. 1). Nanodiamonds are located into a quartz tube which is inserted into the microwave waveguide cavity [7]. This tube is rotated during the exposure to ensure the homogeneity of the hydrogenation treatment over the whole surface of nanodiamonds.

Proper conditions for hydrogenation were previously determined by a sequential study performed in a MPCVD reactor connected to an ultra-high vacuum (UHV) set-up in which surface chemistry could be characterized by XPS [8]. Both High Pressure High Temperature (HPHT) and detonation nanodiamonds were exposed to hydrogen MPCVD plasma. The modifications of surface chemistry were investigated by FTIR and XPS. Both techniques showed a vanishing of oxygenated groups after hydrogenation. C–H stretching bands were also detected on FTIR spectra. X-ray diffraction experiments showed that the mean size of diamond crystal (detonation and HPHT) is conserved after hydrogenation. This confirmed a negligible etching of diamond core by atomic hydrogen during MPCVD exposure at a microwave power of 300 W. The chemical reactivity of the hydrogenated surface was further investigated through functionalization [9]. Three grafting routes specific to hydrogenated diamond surfaces were successfully applied to ND–H (Fig. 2): hydroxylation and alkene graftings under UV illumination and diazonium coupling [10–12]. More details about the surface chemistry of H–NDs will be provided in the paragraph 3. These results well demonstrated that the hydrogenated surface of HPHT nanodiamonds possesses the specific chemical reactivity of bulk diamond with a negative electron affinity (NEA) and the formation of a surface conductive layer (SCL) via adsorption of molecules from the ambient air [13].

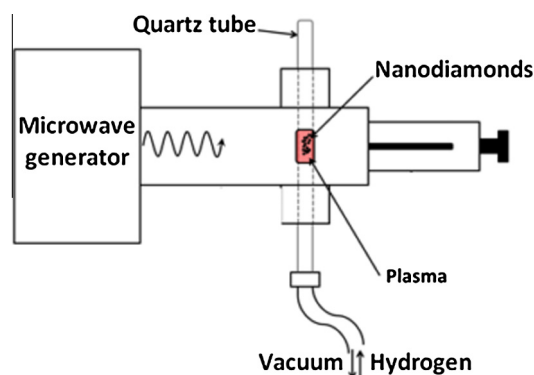


Fig. 1. Home made set-up for plasma hydrogenation of nanodiamonds [7].

The presence of a surface conductive layer (SCL) on nanodiamonds produced by laser synthesis exposed to a hydrogen plasma was then confirmed by Scanning Tunneling Spectroscopy (STS) and Kelvin Force Microscopy (KFM) [14]. After exposure to a MPCVD hydrogen plasma at 620 °C during 2 min or 20 min, nanodiamonds were exposed to humid atmosphere. Isolated nanodiamonds deposited on a silicon substrate were then probed by STS and KFM. A surface conductivity similar to the one occurring on bulk diamond surfaces was evidenced on nanodiamonds with diameter larger than 5 nm. This surface conductivity arises from the combination of the NEA, fingerprint of the hydrogenated surface and the adsorption of molecules at the surface. The shorter hydrogen plasma (2 min) is insufficient to confer a NEA to nanodiamonds. This is related to a poor hydrogenation of the surface. After the longer plasma exposure (20 min), a NEA included between -1.1 eV and -0.8 eV was measured on nanodiamonds with sizes from 16 nm to 5 nm [13].

This result is in line with the high reactivity of ND–H with water molecules which exhibit a higher hydrophilicity compared to ND–COOH according to measurements of water adsorption [15]. The induced surface conductivity was evidenced by XPS. Indeed, hydrogenated nanodiamonds were analyzed by XPS after being suspended in water. An in situ annealing at 400 °C was performed under UHV to desorb adsorbed molecules. The C1s photoemission peak underwent an upshift of 1 eV after annealing [15]. This result is in agreement with the expected downshift reported on hydrogenated bulk diamond exposed to ambient air [16]. More details about the interactions of nanodiamonds with water are discussed in Part 4.

The same plasma approach has been more recently used to achieve radioactive labeling of detonation nanodiamonds. This labeling constitutes a major challenge for bio-applications of nanodiamonds especially to study the in vivo biodistribution and pharmacokinetics [17]. Girard et al. adapted their set-up based on a MPCVD plasma (Fig. 1) replacing hydrogen by tritium [18]. According to the quantification achieved by liquid scintillation, a significant part of tritium atoms, close to 7% of the total number measured on the treated nanodiamonds, is embedded into the diamond core. The corresponding radioactivity ($600 \mu\text{Ci mg}^{-1}$) is largely sufficient to perform biodistribution and pharmacokinetics according to the literature [19]. Indeed, such studies reported a total activity of 1 μCi per mice. To summarize, this plasma treatment provides highly stable ^3H -ND usable for further surface functionalization and in vivo investigations.

Very recently, Kromka et al. reported the use of a diffuse coplanar surface barrier discharge performed at atmospheric pressure at low temperature (70 °C) [20]. Although this treatment was able to significantly modify the surface chemistry of detonation nanodiamonds as shown by FTIR and XPS, it was not sufficiently efficient to remove the non-diamond species surrounding diamond core. Indeed, a significant sp^2 contribution was measured by XPS after the treatment. Moreover, treated nanodiamonds suspended in water still behave a negative zeta potential. As a consequence, C–Hx bands detected in FTIR correspond more to hydrogen

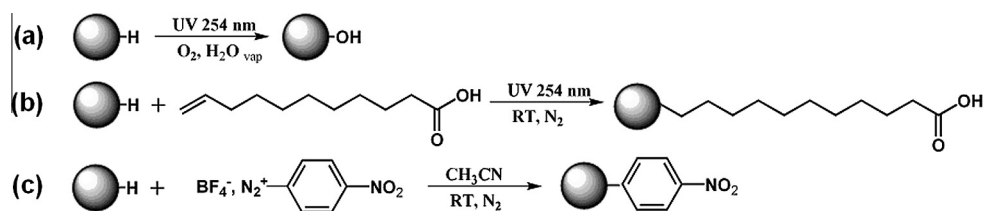


Fig. 2. The three grafting routes applied to hydrogenated HPHT nanodiamonds [9].

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