



Hydrogenation of nanodiamonds using MPCVD: A new route toward organic functionalization

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ARTICLE INFO

Article history:

Received 22 December 2009

Received in revised form 10 March 2010

Accepted 23 March 2010

Available online 30 March 2010

Keywords:

Nanodiamonds

Hydrogenation

Surface analysis

Functionalization

Diazonium

ABSTRACT

Nanodiamonds (NDs) emerge as excellent candidates for biological applications but their functionalization is still an issue. By analogy with hydrogenated diamond layers, an efficient and homogeneous covalent functionalization can be achieved on hydrogenated NDs. Here is reported an efficient new approach to hydrogenate NDs by reducing all various oxygenated groups into C–H terminations. The hydrogenation treatment is performed by exposing the nanoparticles to microwave hydrogen plasma in the gas phase. The hydrogenation of the nanoparticles has been carefully characterized by FTIR and XPS analysis revealing strong modification and homogenization of their entire surface. To validate this hydrogen treatment, functionalization of the NDs has been conducted by using diazonium reactions. An efficient grafting was observed for the hydrogenated NDs compared to the as-received ones.

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1. Introduction

Recent developments in nanosciences and nanotechnologies have shown that diamond nanoparticles or nanodiamonds (NDs) are of high interest owing to their outstanding mechanical and optical properties associated with their good chemical stability [1–3]. Since the demonstration of their low cytotoxicity [4–6], NDs are considered as promising materials for biological applications [7]. Actually, nanodiamonds are studied for drug delivery applications [8]. NDs exhibit also remarkable luminescence properties with emission of great stability and of high quantum yield which originate from color centers (such as Nitrogen-Vacancy centers), naturally present or induced by ion beam irradiations in the diamond lattice [2,9,10]. Consequently, NDs emerge also as excellent candidates for biolabeling applications [6].

For the development of such applications, functionalization of the NDs is required. The carbon surface of diamond constitutes an excellent support for covalent functionalization. However, as reported in the literature, direct covalent functionalization of NDs appears to be a limiting step, since efficient grafting may be restricted by the complex surface of the raw NDs. Mainly due to oxidizing post-synthesis treatments, NDs are covered by a wide variety of oxygenated functions: hydroxyl, ether, ketones or carboxylic acid groups [10]. This scattered superficial chemistry prevents an efficient

and homogenous functionalization due to different reactivity of these various oxygenated groups.

Different experimental pathways have been explored to better control the surface termination of NDs. The first one is the oxidative treatment of NDs with strong acids leading to the formation of COOH groups on the surface which can then react with alcohols or amines derivatives [11–13]. Another approach reported by Krueger et al. [10] consists in reducing all oxygen-containing surface groups to OH functions with borane, then allowing the grafting of a variety of silanes [14] or long alkyl chains [15]. Halogenation of NDs has been also reported such as the thermal fluorination of detonation diamond by Khabashesku and coworkers [16], and the cold-plasma functionalization used by Ray et al. [17]. Fluorinated NDs can then react with nucleophilic reagents in substitution reactions leading to amino or acid terminations [16].

By analogy with diamond films, another promising way to homogenize NDs surface is the hydrogenation. Indeed, by reducing all oxygenated terminations into C–H groups, this treatment ensures a reproducible and versatile surface for further functionalization. Furthermore, hydrogenated terminations confer on diamond films specific electronic properties, allowing particular grafting approaches based on physico-chemical activations. In pioneering works, Hamers and coworkers [18,19] reported on functionalization of hydrogenated diamond surface by photochemical reaction under UV illumination with a long-chain unsaturated amine, being the first step to DNA-modified diamond surface. Based on the same photochemical method, Christiaens and coworkers [20] overcame the problem of insufficient carboxylation by attaching fatty acid chains to the diamond surface and created a universal coupler for amino groups. Still on hydrogenated diamond

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surfaces, Lud et al. [21] presented the grafting of one monolayer of nitrophenyl by using the corresponding diazonium salt. Spontaneous reaction of diazonium derivatives on diamond hydrogenated surfaces was also reported by Boukherroub and coworkers in the presence of sodium dodecyl sulfate [22]. In the same way, Shul et al. [23] reported on solvent-free functionalization of hydrogenated surface by aryldiazonium salts in ionic liquids, and suggested that the electron necessary for reduction of diazonium salt are most likely provided by the hydrogenated diamond surface.

By analogy with these works, a large field of functionalization methods is potentially offered to hydrogenated NDs (H-NDs). Indeed, first promising results concerning surface grafting of hydrogenated particles have been recently reported. Yeap et al. [24] has described the functionalization of NDs with aryl organics using Suzuki coupling reaction, starting from partially hydrogenated NDs (presence of hydroxyl groups at the surface) and they showed that diazonium coupling can occur on these NDs. Regarding electronic properties provided by hydrogenated terminations, a detailed study on hydrogenated micrometric diamond powder was conducted by Chakrapani et al. [25]. They demonstrated an electron transfer from the diamond to the surface, deduced from zeta potential measurements, leading to a surface conductivity. It would be interesting to know whether such specific chemical and electronic properties of hydrogenated diamond surfaces can be also obtained on hydrogenated NDs.

To take advantage of the promising properties of H-NDs, the initial treatment conferring the hydrogenated terminations is crucial and has to be carefully optimized. In the literature, only few example of hydrogen treatments performed on NDs deposited onto substrates have been reported, using either atomic hydrogen exposure under ultra-high vacuum (UHV) [26,27] or microwave hydrogen plasma [24,28]. These methods seem to be efficient in terms of surface modification but lead only to a partial hydrogenation of the NDs surface. Moreover, some chemical interactions can take place between NDs and the substrate during the hydrogenation treatment [28]. To the best of our knowledge, there is no reported method providing hydrogenation of the whole NDs surface.

Here, we report on a new approach allowing the full hydrogenation of NDs by exposition to hydrogen Microwave Plasma Chemical Vapor Deposition (MPCVD). NDs are treated in the gas phase allowing the modification of their whole surface by reducing oxygenated terminations into hydrogenated ones. Furthermore, the present method is able to treat a large amount of NDs simultaneously, (hundreds mg), which is a prerequisite to a meaningful surface functionalization. Two kinds of NDs have been studied which are produced either by High Pressure High Temperature (HPHT) or detonation processes. These NDs mainly differ by their size and the graphitic shells surrounding the sp^3 core for detonation NDs [29]. Surface modifications of the NDs induced by the hydrogen plasma exposure have been carefully characterized using X-ray Photoelectron Spectroscopy (XPS) and Fourier Transformed Infra-Red Spectroscopy (FTIR). Finally, to validate the hydrogen treatment, functionalization on these H-NDs has been conducted by using diazonium reactions.

2. Experimental

2.1. Chemicals

High Pressure High Temperature (HPHT) NDs (mean diameter: 50 nm) were purchased from Van Moppes (Syndia® SYP 0-0.05). Detonation diamond NDs (mean diameter of primary particles: 5 nm) were provided by NanoCarbon Research Institute Ltd. Acetonitrile (Riedel-De Haën), pentane (VWR) and 4-nitrophenyldiazonium tetrafluoroborate (Aldrich) were used as received.

2.2. MPCVD hydrogenation

NDs were used as-received. 100 mg of NDs was deposited in a quartz cartridge which was introduced in a quartz tube. This system was introduced into the microwave waveguide cavity (Fig. 1). After a pumping stage, the hydrogen was injected up to 10 mbar. Hydrogen plasma was generated in the quartz tube with a microwave power of 300 W. To limit the temperature of NDs, the quartz cartridge was sequentially removed from the waveguide for few seconds. A rotation of the quartz tube was also applied to mix and homogenize the NDs in the hydrogen plasma. After exposure, H-NDs were collected in dry pentane under hydrogen flux and stored under controlled atmosphere to avoid any spontaneous surface oxidation by air.

2.3. Functionalization

20 mg of as-received or hydrogenated HPHT and detonation nanodiamonds were reacted with 60 mg ($2.5 \cdot 10^{-4}$ mol) of 4-nitrophenyldiazonium tetrafluoroborate in 25 mL of acetonitrile during 12 h. All experiments were conducted under vigorous stirring and under controlled atmosphere. After reaction, NDs were washed by 5 successive centrifugation-redispersion cycles in acetonitrile and then the solid residue was dried under vacuum.

2.4. Characterizations

XPS analyses were performed using an Omicron XPS spectrometer equipped with an Al $K\alpha$ monochromatized anode ($h\nu = 1486.6$ eV). The binding energy scale was calibrated versus the Au 4f 7/2 peak located at 84.0 eV [30]. The penetration depths are given by the inelastic mean free paths for C1s core levels, close to 3 nm [31]. Curve fitting procedure was performed to extract the components in the C1s spectra, using a fixed Gaussian/Lorentzian ratio of 30%. Peak areas were determined following the Shirley's inelastic background subtraction method. Atomic ratios were calculated from the integrated intensities of core levels after photoionization cross-section corrections. The component ratios C_x/C_{total} correspond to the integrated intensity of each peak C_x over the total area of the C1s spectrum. To avoid air exposure, immediately after hydrogenation a small amount (few mg) of H-NDs (HPHT or detonation) covered with a drop of pentane was deposited on the sample holder and introduced directly in the UHV set-up equipped for surface analysis.

FT-IR spectra were measured in a transmission mode using a Thermo Nicolet 8700 spectrometer. KBr pellets (150 mg) were prepared using 5 mg of as-received, H-NDs (immediately after hydrogenation) or functionalized NDs. Background signal was recorded using a pure KBr pellet. Depending on the experiment, KBr pellets containing or not NDs were dried in a dessicator for one day under primary vacuum.

Powder X-ray diffraction patterns were acquired on a X'Pert Philips diffractometer (40 kV, 40 mA) with $CuK\alpha$ radiation ($\lambda = 0.154056$ nm).

3. Results and discussions

3.1. MPCVD hydrogenation

Hydrogenation of the diamond nanoparticles was performed on as-received HPHT and detonation NDs using MPCVD hydrogen plasma. The experimental set-up is shown on Fig. 1 and described in experimental section. FTIR spectra of as-received and hydrogenated NDs are reported on Fig. 2. For as-received HPHT NDs (Fig. 2a), a broad band is observed at 1775 cm^{-1} characteristic of C=O stretching band involved in carboxylic acid groups and anhydride functionalities [32]. This band is less intense for as-received detonation NDs (Fig. 2b), and due to their smaller size the signal is shifted to 1730 cm^{-1} [33]. For

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