Vibrational Spectroscopy 83 (2016) 108–114

Contents lists available at ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec

Oxidation and reduction of nanodiamond particles in colloidal solutions by laser irradiation or radio-frequency plasma treatment☆

Halyna Kozak[a,*], Anna Artemenko[a], Jan Čermák[a], Vladimir Švrček[b], Alexander Kromka[a], Bohuslav Rezek[a,c]

[a] Institute of Physics ASCR, Cukrovarnicka 10, 16200 Prague 6, Czech Republic
[b] Research Center for Photovoltaics v, AIST, Tsukuba 305-8568, Japan
[c] Faculty of Electrical Engineering, Czech Technical University, Technicka 2, 16627 Prague, Czech Republic

ARTICLE INFO

Article history:
Received 12 November 2015
Received in revised form 16 January 2016
Accepted 27 January 2016
Available online 29 January 2016

Keywords:
Nanodiamonds
GAR-FTIR
Laser
RF plasma
XPS
Zeta-potential
KPFM

ABSTRACT

Functionalized nanodiamond particles (NDs) represent carbon nanomaterial with unique properties for various applications. Here we report on a new approach to surface modification of NDs by their exposure to radio frequency (RF) plasma or laser irradiation (LI) plasma directly in aqueous solution. By using grazing angle reflectance Fourier transform infrared spectroscopy and supporting analysis by X-ray photoelectron spectroscopy, zeta-potential, and Kelvin force microscopy we show that surface chemistry of NDs produced by detonation process (DNDs) or high-pressure high-temperature process (HPHT NDs) works in different way. Moieties on as-received NDs are dominated by COOH and C—O—C groups due to wet chemical cleaning procedures. On DNDs, both RF and LA treatment lead to removal of sp^2 shell and additional oxidation of the surface to C— O—C groups. On HPHT NDs the RF treatment leads to reduction of C—O—C groups that are transformed into C—OH and C—H moieties. Thus at least partial hydrogenation of colloidal HPHT NDs seems feasible.

1. Introduction

Nanodiamond particles (NDs) have recently attracted wide interest in the field of biotechnologies and biomedical applications because of excellent properties such as low toxicity, good biocompatibility, possibility of its surface functionalization, and their ability to fluoresce [1,2]. NDs were used for drug delivery, biosensors, bioimaging, implant coatings, or even artificial substrates for tissue engineering [3–5]. Moreover, recently we reported on an antibacterial activity of NDs, which was influenced not only by their concentration but also by their surface chemistry and size [6,7].

Appropriate application of NDs requires a well-defined surface termination as their properties differ significantly in the chemical affinity. Moreover, surface functional groups of NDs have a strong influence on their aggregation behaviour in aqueous solutions. The pristine NDs represent a complex mix of diamond core (sp^3 hybridization) and graphitic soot shell (sp^2 hybridization). Hence, treatment in strong acids is used to remove graphitic soot and different impurities from the NDs surface [1,8]. As a result the surface of pristine NDs is covered with variety of functional groups such as COOH, C—H, OH, C=O, and others [8]. Purified NDs are subsequently used as a starting material for further surface functionalization. The modification of NDs has been mostly performed by different gases in oxidative (e.g. air, oxygen plasma), reductive (e.g. hydrogen, methane), or inert (nitrogen, vacuum) atmospheres. For example, air-annealing at elevated temperatures or oxygen plasma treatment were shown as oxidative methods for selective etching of non-diamond carbon and obtaining of NDs surface dominated by oxygen containing functional groups [9,10]. We have recently reported that the air-annealed NDs are chemically stable in air in similarity to bulk diamond [10]. Hydrogen treatment of NDs in microwave plasma was used to homogenize NDs surface and passivate it by hydrogen atoms [11]. Recently a new approach for plasma-assisted NDs hydrogenation at temperatures below 100 °C was reported by Kromka et al. [12]. Other methods to functionalize NDs include for example fluorination and amination [13,14]. Functionalized NDs are used as the fundamental basis for further functionalization with aliphatic and polar/ionic organic groups for different fields of applications. Biomedical applications commonly require NDs to be delivered and used in aqueous solutions. Although a lot of studies have been published on modification of NDs, study of their

☆ Selected paper from 8th International Conference on Advanced Vibrational Spectroscopy, 12–17 July 2015, Vienna, Austria.

* Corresponding author.
E-mail address: kozak@fzu.cz (H. Kozak).

http://dx.doi.org/10.1016/j.vibspec.2016.01.010
0924-2031/

plasma-chemical modification directly in colloidal solutions is still missing despite being of high practical importance.

In this contribution we report on a novel approach to NDs surface modification directly in colloids by two different methods: (a) pulsed laser irradiation (LI) system used to generate plasma inside the colloid; (b) radio-frequency (RF) microplasma jetting from a quartz capillary into the colloid. We compare and discuss the surface chemistry of two different kinds of NDs produced either by detonation process (DNDs) or high-pressure high-temperature (HPHT). The NDs surface chemistry before and after chemical modifications is analysed by grazing angle reflectance Fourier transform infrared (GAR-FTIR) spectroscopy and corroborated by X-ray photoelectron spectroscopy, Kelvin probe force microscopy, and dynamic light scattering measurements. We show that surface chemistry of DNDs and HPHT NDs works in different way, resulting in surface oxidation as well as reduction, thereby opening prospects for hydrogenation of NDs in colloidal solutions.

2. Materials and methods

Detonation nanodiamond (DND) particles with a nominal average size of 5 nm were provided by New Metals and Chemicals Corp., Ltd. (Kyobashi, Japan). Monocrystalline synthetic NDs with a nominal average size of 18 nm produced by HPHT method were purchased from Microdiamant AG (Lengwil, Switzerland). Both types of NDs were dispersed in water in the as-received condition. Surface modification of colloidal NDs proceeded by two different methods. The first method so called LI is based on a laser beam (Kr: F, 245 nm, 20 Hz, 130 mJ per pulse), which was used for 45 min to generate a plasma in the colloid of NDs. The laser beam was focused onto a 3 mm diameter spot on the liquid surface by a lens with a focal length of 250 mm. During the irradiation, the glass container was closed and rotated. In more details this method is described in [15]. In the second method the RF microplasma was generated in a quartz capillary and "jetted" out onto the NDs colloid. The applied power at the power supply was kept at 60 W (450 MHz) for 15 min. The distance between the end of the quartz capillary and the surface of the colloid was initially adjusted at about 2 mm, however it was increased up to 2.5 mm over time as water evaporated during processing [16].

The changes in the functional groups on the NDs surface before and after plasma treatments were studied by GAR-FTIR spectroscopy. IR spectra were measured using Thermo Nicolet 8700 spectrometer equipped with KBr beamsplitter and MCT detector cooled by liquid nitrogen [10]. For GAR-FTIR measurements 120 μL of the NDs dispersion was dropped on the Au mirror and dried at 100 °C for 3 min to evaporate water. GAR-FTIR spectra were collected also after 3 days of NDs drying in vacuum in order to reveal details that were otherwise hidden in water-related bands. Additional analysis was performed to corroborate interpretation of the GAR-FTIR spectra.

Chemical composition of NDs was estimated by X-ray photoelectron spectroscopy (XPS) using spectrometer (Kratos, AXIS Supra) equipped with a hemispherical analyser and a monochromatic Al Kα X-ray source (1486.6 eV). The XPS spectra were acquired from the area of 700 × 300 μm^2. The XPS take-off angle was 90°. The survey XPS spectra were recorded with the pass energy of 80 eV, the high resolution scans with the pass energy of 20 eV. The Casa XPS software with Shirley background correction procedure and Gaussian line shapes of variable widths were used for spectra processing. The samples for XPS analysis were prepared by drop casting the suspension (NDs in water) on the polished Si substrates. Then this suspension was dried at 100 °C for 3 min in the open air. The NDs layer was thick enough to avoid an appearance of the signal from the Si substrate in the XPS spectra.

Zeta-potentials and hydrodynamic diameters of NDs in aqueus solutions were evaluated from dynamic light-scattering (DLS) measurements at 25 °C using a Nano-ZS (Malvern, UK) equipped

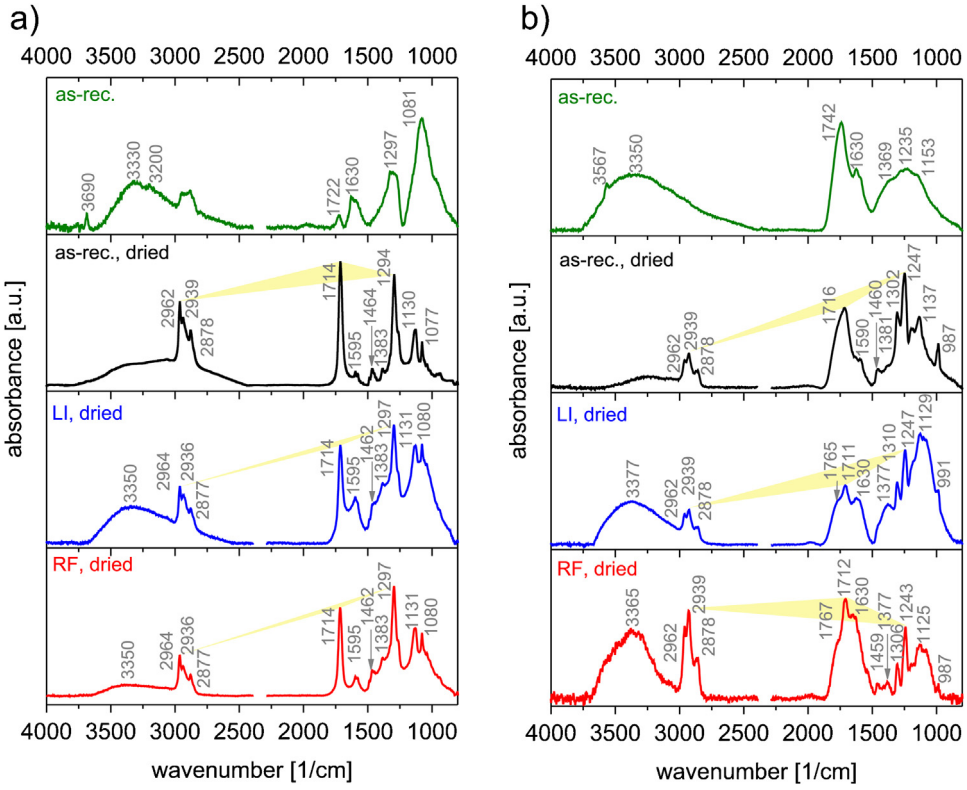

Fig. 1. GAR-FTIR absorbance spectra of a) DND and b) HPHT nanodiamond particles before and after plasma treatments in colloidal solutions. The top row shows the spectra of NDs after drying in air at 100 °C. Spectra with label "dried" are related to NDs after drying in vacuum for 3 days.