Interpretation of the C=O band of modified diamond nanoparticles by means of DFT theory

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Abstract

Diamond nanoparticles (DNPs) are an interesting class of nanomaterials, which has many unique properties. Their applications in medicine and molecular biology have been mentioned. The DNPs were reviewed in sense of their surface chemistry and a range of analytic techniques was pointed out. The experimental analysis can be enhanced by theoretical models based on the first principles. An approach to theoretical analysis of infrared spectra was introduced. As an example, a part of FTIR spectra of the oxidized DNPs was interpreted by means of the DFT theory. The calculation of the C=O stretch vibrational frequencies of carboxylic and anhydride groups on certain model clusters enabled to explain the shift and splitting of the measured spectral bands.

Keywords: diamond nanoparticles, functionalized diamond surface, density functional theory, vibrational spectra, FTIR

1. INTRODUCTION

1.1 Diamond nanoparticles – new class of functional materials

Diamond is an outstanding material for many fields of applications due to its superior properties, which include excellent mechanical, optical and electrical properties, good biocompatibility, chemical stability, and the resistance to harsh environments. Diamond nanoparticles (DNPs) represent a highly attractive class of nanomaterials which inherit some of the superior properties of bulk diamond. Moreover, they possess several biologically significant properties that make them promising for biomedical applications. For example, fluorescent DNPs combine the small size, high photostability, bright multicolour fluorescence with biocompatibility, non-toxicity and rich surface chemistry, which means that they have a potential as biomarkers (photoluminescence), drug and gene delivery systems (functionalized surface), and other biomedical applications [1]. Our microbiological studies have also proven DNPs antibacterial activity against *Escherichia coli* and *Bacillus subtilis* [2], [3]. The antibacterial activity was significantly influenced by their surface termination or even size.

One of the main advantages of DNPs besides photoluminescence, low toxicity, and biocompatibility is the possibility to control their surface on atomic level. The hydrophilic surface of DNPs with dominated hydroxyl, carboxyl, carbonyl or other groups can be obtained by thermal annealing, ozone, RF plasma and wet chemical treatments [2]–[4]. Hydrogen treatment of DNPs in microwave plasma resulted in the saturation of their dangling bonds with hydrogen and they revealed hydrophobic properties [5]. Graphitized DNPs were achieved after vacuum

Fig. 1. Scheme of the targeted functionalized process for desired application.

annealing at temperatures about 750 ˚C [6]. Depending on the DNPs surface properties a wide range of bioactive molecules can be grafted onto their surface. For example DNPs with hydrophilic surface is very
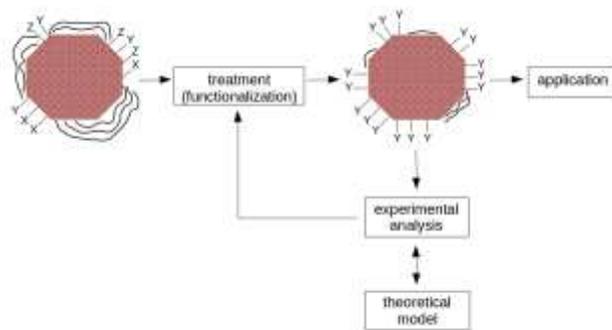
attractive for grafting of silanes [7], long alkyl chains [8], or dopamine derivatives [9], whereas hydrogenated DNPs are efficiently grafted with alkenes using photochemical reaction and a spontaneous coupling with aryldiazonium salts [10].

Apparently, a well-defined surface modification of DNPs by employing a reliable and reproducible technological process is the most important task for their industrial applications. The overall procedure includes not only the DNPs treatment but also their characterization by means of analytic techniques, and possibly enhanced by theoretical models (see Fig. 1).

1.2 Characterization of DNP surface

The most commonly used techniques for DNPs surface chemistry characterization include the X-ray photoelectron spectroscopy, Raman spectroscopy, Kelvin force microscopy, and Fourier transform infrared spectroscopy (FTIR). The FTIR is a powerful method, which has been widely used to detect changes in the surface chemistry of functionalized DNPs. The surface related infrared (IR) absorption spectra has been acquired so far mostly on functionalized ultra-dispersed DNPs using a transmittance or diffuse reflection spectroscopy [11], [12]. Such methods are based on KBr pellets with dispersed DNPs. This approach has several disadvantages, caused by the pellets hygroscopicity and strong light scattering [13]. Recently we have shown that the vibrations of the functional groups on the functionalized DNPs can be detected well in reflection mode by the grazing angle reflection (GAR) spectroscopy with p-polarized light at Brewster's angle of incidence [14]. We showed that GAR-FTIR using bare Au mirrors can detect with high resolution and sensitivity the changes in functional groups on chemically modified DNPs, including their stability in the air [14].

1.3 Theoretical studies on DNP surface

First-principle calculations can be used for fundamental understanding of the surface and internal structure of the functionalized DNPs. Properties like the surface structure and stability [15]–[18], reactivity [19]–[22] or optical properties [23] of DNPs were computed. Although some theoretical studies treated the models of DNPs of a "nearly realistic" size (1-5 nm) with functionalized surface [24]–[26], the computationally effective calculations are usually limited to smaller fragments. In such way, the structure of oxidized [27], [28] and halogenated [29] surfaces was computed.

Despite its easy accessibility and reputation, the first-principle calculations based on the density functional theory (DFT) are not routinely used for the modelling of vibrational spectra of diamond surfaces. The reason of this fact lies probably in a large variety of functional groups as they occur on the diamond surface after wet chemical treatment [30]. However, a comparison of a certain measured spectral band with the computed vibrational frequencies of the most probable atomic arrangements can exclude or confirm the frequency assignment and greatly help to interpret the measured IR spectra. For example, the computations can help to decide if the measured C-H stretch vibrations correspond to the hydrogen termination of bare diamond surface dangling bonds or to small hydrocarbon groups chemisorbed on the surface.

Despite the fact that the infrared spectra for hydrogenated DNPs were computed by several authors, no works on DFT calculations of vibrations of oxygen- or nitrogen functionalities on the diamond surface were found in the open literature. This work is aimed to fill out this gap. In the present work, the theoretical vibrational analysis of the carbonyl functions on the oxidized DNPs was made and compared with the measured FTIR spectra.

2. EXPERIMENTAL AND THEORETICAL APPROACH

The DNPs were oxidized by two different techniques – in the RF oxygen plasma and by annealing in air. The

duration of plasma oxidation was 10 or 40 min, and the annealing was conducted at 450 °C for 30 min. The SEM image of the as-received DNPs deposited on polished Si substrate is shown in Fig. 2. It indicates that DNPs form small aggregates. We were not able to clearly identify the separated DNPs using our SEM setup. However, KFM measurements confirmed the presence of single DNPs [16]. The IR spectra of DNPs were taken and compared with the spectra of the as-received DNPs. Further details can be found in our paper [14].

The theoretical approach can be described as follows. Since the XRD spectroscopy [16] unveiled surfaces preferentially with the {111} orientation, we restricted our study to this surface orientation. First, the cluster of two atomic layers of the {111} oriented diamond surface with 49 carbon atoms terminated by hydrogens was geometrically optimized on the B3LYP/6-31G* level of theory. Then, the bottom layer of carbons was removed and replaced by hydrogens. Last, the functional groups were placed on the surface, geometrically optimized and vibrations were computed. The computations were conducted under the commercially available software Gaussian G09 [31].
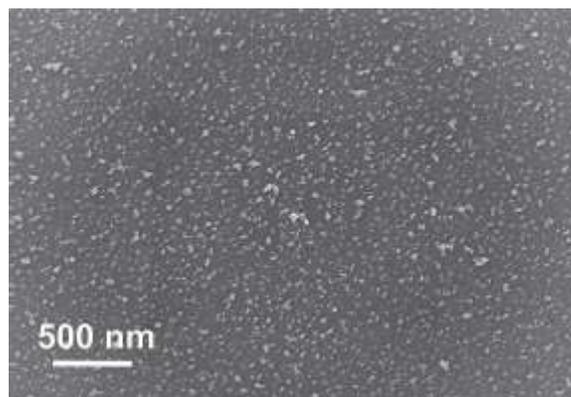

Fig. 2. SEM image of DNPs deposited on polished Si substrate.

3. RESULTS AND DISSCUSSION

Figure 3 shows measured C=O spectral band (lines with points) of the oxidized DNPs together with the theoretical results. The apparent changes in position and shape of the C=O band of carbonyl groups when using different oxidizing methods are not so far fully understood. The oxidation of diamond surface may lead to a variety of carbonyl compounds, including aldehydes, ketones, carboxylic acids, esters, anhydrides, amides, lactams [30]. Since we restricted our calculations to the {111} surfaces, we can exclude ketones due to missing dimer carbon, and aldehydes and amides which are too far from the main peaks of the experimental C=O band. The carboxylic (-COOH) and anhydride (-OCOCO-) groups were chosen as the most probably contributing to the spectral band.

First, the influence of surface coverage by carboxylic groups was investigated. In this, one hydrogen termination was replaced by carboxylic group and then one to three more groups of the same kind were successively added to the closest possible place. The computed frequency of a single carboxyl coincide very well with the spectral peak of the as-recieved DNPs. As more carboxyls are added, new, higher frequencies appear in the calculated spectra, but this shift (up to 45 cm^{-1}) is not sufficient to describe the changes in measured spectral band. The most split band was computed at the most packed arrangement involving four carboxylic groups, which requires tilting of the carboxyls against each other. The shape of the experimental C=O bands for plasma-oxidized DNPs resemble rather the well-known double band of carboxylic anhydride [32] than only mutually influenced carboxyl groups. The similar analysis of increasing surface coverage was then conducted with the anhydride functionalities. The computed frequencies of the strongest, antisymmetric anhydride mode are in a very good agreement with the measured peak (1763-75 cm^{-1}). To be specific, the computations of two anhydrides coincided with the spectra of 10-min plasma treated DNPs and three close together anhydrides with the 40-min treated DNPs. The computed positions of the weaker, symmetric mode (1842 cm^{-1} in the measurement) were by 16-30 cm^{-1} lower than measured. The calculated frequencies are plotted together with the measured spectra in Fig. 3.

Based on the computations, we suppose that the oxidation in oxygen plasma increases the initially low coverage (as-received sample) of the DNP surface with carboxylic groups and further their closer packing leads to the condensation of neighboring carboxyls to the anhydrides. On the other hand, the measured spectral C=O band

of the annealed particles was not reproduced by the used models. Further analysis, including also other spectral bands is needed to get better understanding of the undergone changes in the annealing experiment.

The relatively far-distant shoulder around 1900 cm^{-1} on the spectra of plasma-oxidized samples was also not reproduced by the DFT calculations. One of the considered phenomenons is the DNPs clustering via creating the anhydride bridges between neighboring DNPs. Such an arrangement could bring the oxygen atoms close to the surface, cause the rearrangement of the C=O bonds and increasing their vibrational frequency. The calculations which are now in progress support this possibility.
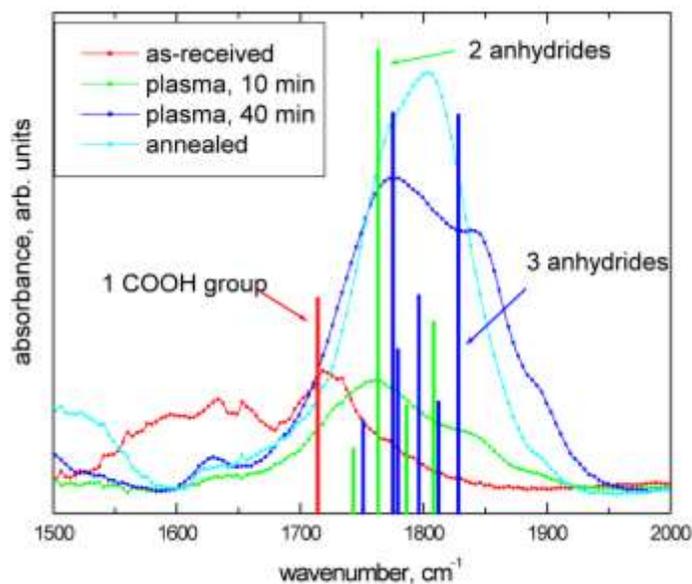

Fig. 3. Measured C=O spectral band (lines with points) of the oxidized DNPs together with theoretical results. The calculated C=O stretch vibration frequencies are denoted for the single carboxylic group, two anhydride and three anhydride groups.

4. CONCLUSIONS

Advance properties of DNPs were reviewed regarding their promising applications in life science which were discussed regarding their specific surface chemistries. The capabilities of first-principle theories in DNPs research were summarized and an approach to theoretical analysis of vibrational spectra was introduced. As an example, a part of experimentally measured GAR-FTIR spectra of oxidized DNPs was correlated by means of the DFT theory. The calculation of the C=O stretch vibrational frequencies of carboxylic and anhydride groups on certain model clusters enabled to explain the shift and splitting of the measured spectral bands. The computed frequency of a single carboxyl group on the {111} diamond surface coincided very well with the spectral peak of the as-received DNPs. The calculation of anhydride vibrations on diamond confirmed that the treatment in oxygen plasma promotes a strong oxidation leading to the condensation of new carboxyl groups to anhydrides.

ACKNOWLEDGEMENT

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