Diamond/carbon nanotube composites: Raman, FTIR and XPS spectroscopic studies

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ABSTRACT

As long as the carbon family materials are pristine, powerful methods for their individual characterization have been established and well understood. However, as soon as these materials contain a mixture of sp² and sp³ hybridized carbons, the spectroscopic characterization becomes challenging. In this paper we present on some aspects of multiply spectroscopic characterizations of sp²-sp³ carbon heterosystems, which can play an important role for their correct structural assignment. We study a composite of single-wall carbon nanotubes (SWCNT) with diamond nanoparticles and a SWCNT paper coated with nanocrystalline diamond films. The SWCNT paper serves here as a reference. We evaluate the surface free energy measured by contact angle technique, morphology imaged by scanning electron microscopy and the chemical composition determined by X-ray photoelectron spectroscopy, Raman spectroscopy at different excitation wavelengths and by attenuated total reflection (ATR) Fourier Transform Infrared spectroscopy (FTIR) using different ZnSe ATR prisms. We demonstrate that, because of the resonant nature of Raman process in SWCNTs, the particular conditions at Raman measurement (laser excitation wavelength, laser intensity) strongly influence the measured spectra of the sp²-sp³ hybridized heterosystems. We also show how the dimensions of the ATR prism affect the results of the FTIR measurements of the SWCNT papers.

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1. Introduction

In the last two and half decades, a great attention has been dedicated to carbon for its ability to form fascinating materials with different dimensionalities, given by the variable hybridization of carbon atomic orbitals. Graphene-based nanostructures such as carbon nanotubes (CNTs) or graphene sheets can be assembled into free-standing membranes, known as buckypapers (BPs), and used for numerous applications [1–5]. The outstanding properties of the individual graphene-based nanoparticles are retained only to a certain extent when they form BPs. For example, the individual metallic nanotubes can carry an electrical current density of 4 × 10⁹ A/cm² [6], whereas the value decreases down to 10⁶ A/cm² in the CNT membranes due to tube-to-tube resistance [7]. Nevertheless, this current density can well compete with a typical current density value 3.6 × 10⁵ A/cm² of the 35 μm thick copper leads in a printed circuit [8]. The BPs can be easily formed from a mixture of different carbon materials combining and modifying the properties of BPs. Mixing SWCNTs with graphene oxide led to a significant improvement of the electrical and mechanical performances [9]. Raman spectroscopy provided clear evidence for the charge transfer mechanism responsible for the rather surprising experimental observations.

Recently, the combination of CNTs and diamond nanoparticles...
which can not only distinguish the type of carbon hybridization conditions. The signal originated from one carbon hybridized form carbon nanotube composites is still a challenge because the results bon structures. Contrary, the complex characterization of diamond/carbon nanotube composites can also be promising as thermal interface material or highly sensitive gas-sensing device. The compact 3D matrix can be further easily exposed to the high temperature and high growth rate CVD deposition of boron-doped diamond or diamond-like carbon films. Thus a possible application as electrodes for electrochemical redox cells of huge area and extremely large capacitance can be observed [5,15–18]. However, for such composites, the complex spectroscopic characterization is still demanded.

In our earlier studies, we investigated the growth of diamond film on single-wall carbon nanotube (SWCNT) BPs by employing three different chemical vapour deposition (CVD) systems [19]. We found that the diamond growth is affected by the different process conditions characteristic for each CVD process and only the pulsed linear antenna microwave plasma (PLAMW) CVD process allowed the penetration of the activated growth species into the volume of the SWCNT BP. Moreover, PLAMW CVD is characterized by a so-called “cold plasma” and allows the diamond growth at low deposition temperatures [20,21].

The bulk carbon structures such as diamond, graphite, as well as the low-dimensional allotropes graphene, carbon nanotubes and fullerenes can be clearly distinguished thanks to their unique spectroscopic features - fingerprints of each of the particular carbon structures. Contrary, the complex characterization of diamond/carbon nanotube composites is still a challenge because the results from the applied analyses strongly depend on the measurement conditions. The signal originated from one carbon hybridized form can be easily hidden in the features of the other carbon form. Raman spectroscopy is a sensitive technique for carbon materials, which can not only distinguish the type of carbon hybridization \( (\text{sp}^2, \text{sp}^3, \text{sp}^3) \) with a high precision but also the level of the structural disorder [22]. The laser intensity as well as the used laser excitation wavelength are crucial parameters which determine the spectral features in particular measurements [23,24]. Next, Fourier transform infrared spectroscopy (FTIR) as a complementary technique to Raman spectroscopy can recognize the graphitic nature of the carbon based composites and is sensitive to hetero-nuclear functional group vibrations and polar bonds. On the other hand, the FTIR method has constraints on sample thickness, uniformity and homogeneity to avoid saturation [25]. In contrast to Raman and FTIR measurements, the X-ray photoelectron spectroscopy (XPS) detects the signal coming only from the top of the sample surface. Due to this limitation the standard XPS is not able to investigate the whole sample volume but it is suitable for identifying the \( \text{sp}^2/\text{sp}^3 \) ratio and chemical bonds changes on the sample surface. Therefore, for a deep and accurate characterization of the carbon composites a systematic study is needed, which involves correlation of the measured data from several complementary spectroscopic techniques.

In this contribution we report on a comprehensive experimental investigation of the free-standing \( \text{sp}^2/\text{sp}^3 \) carbon based hybrid composites by SEM, contact angle measurement as well as Raman, FTIR and XPS spectroscopies. Outcomes of the multiply analytical techniques are further correlated and discussed.

2. Experimental part

2.1. Materials and preparation

Three kinds of carbon forms were used and studied: i) bare buckypaper prepared from single-wall carbon nanotubes (SWCNT BP), ii) SWCNT BP with incorporated diamond nanoparticles (DNPs) and iii) SWCNT BP ingrown/overgrown with nanocrystalline diamond (NCD). The details on the fabrication procedure of SWCNTs as well as bare SWCNT BPs are described in Ref. [26]. Briefly, SWCNTs were prepared by laser ablation method and dispersed in n-methyl pyrrolidone (NMP) solution. The dispersed solution was filtered through the nylon membrane by vacuum filtration (i) without (bare SWCNT BP) or (ii) with mixed diamond nanoparticles (monocrystalline synthetic diamond powder, Microdiamant AG, Lengwil, Switzerland, grains size up to 200 nm) to prepare SWCNT BP/DNPs heterostructures. The thickness of such prepared BPs was about 12 μm. Further, SWCNT BP/DNPs sample was loaded in the PLAMW CVD system. The diamond growth was performed for 36 h at a constant total gas pressure of 10 Pa at 5% of CH₄ and 20% of CO₂ in hydrogen, microwave power of \( 2 \times 1.7 \) kW and substrate temperature of 400 °C. During the CVD process, the BPs were positioned in the vertical direction (perpendicularly to the holder) to achieve the diamond growth on both sides of the BP substrate.

2.2. Materials characterization

2.2.1. Raman spectroscopy

Raman spectra of the prepared samples were acquired by Renishaw InVia Reflex Raman spectrometer equipped with He-Cd laser with excitation wavelengths of 325 (UV) and 442 (blue) nm, and Nd:YAG diode laser with 785 (IR) nm. In addition, the spectra were also evaluated by the Raman spectrometer Jobin-Yvon LabRam 300 equipped with a He-Ne laser with excitation wavelength of 633 nm (red). For the UV laser measurements we used a 40× objective and the total laser power at the sample was 0.3 mW. For the measurements with blue (8.25 mW), red (4 mW) and IR (103 mW) lasers a 50× objective was exploited. Before the measurements, the Raman spectrometers were calibrated with respect to the silicon peak (520.7 cm⁻¹). The accumulation time was set to 30 s for all measurements.

2.2.2. FTIR analysis

The attenuated total reflection (ATR) FTIR measurements were performed by Thermo Nicolet Nexus 870 FTIR spectrophotometer in two different setup configurations using: i) thick 6 internal reflections ZnSe ATR prism with dimensions of \( 6 \times 10 \times 72 \) mm² (height, width and length) and ii) custom-made accessory allowing to accommodate a thin ZnSe ATR prism with dimensions of \( 2 \times 8 \times 50 \) mm³ and about 25 internal reflections [27]. The analysed samples were loaded onto the ATR prism by different ways. The bare SWCNTs diluted by surfactant (NMP) was applied by a drop and dry technique when the dilution was dripped to a prism heated above boiling temperature of the solution (220 °C). The sample of DNPs diluted in deionized water was applied in the form of large droplet covering almost whole prism and let dry. In this case, the prism was heated to a temperature of 90 °C. Samples of buckypapers (SWCNT BP, SWCNT BP/DNPs and SWCNT BP/NCD) with the dimension of about 5 × 10 mm² were pressed to the ATR prism to enhance their contact to the prism (i.e. the light interaction).
2.2.3. XPS analysis

The chemical composition of the samples surface was further characterized by X-ray photoelectron spectroscopy (XPS). The XPS system is equipped with a multi-channel hemispherical electrostatic analyser (Phoibos 150, Specs) and a dual (Al/Mg) anode X-ray source. The Al Kα X-ray source (1486.6 eV, Specs) was used with the incidence angle of 45° to the surface plane. Survey spectra were acquired at 40 eV pass energy and the high resolution spectra were measured at 10 eV pass. The XPS spectra were acquired at a constant take-off angle of 90°. The CasaXPS software using a linear baseline and Gaussian line shapes of variable widths was applied for spectra processing. XPS peak positions were determined with an accuracy of 0.2 eV.

2.2.4. SEM measurements

The surface morphology of the samples was analysed using a field-emission scanning electron microscopy gun operating in secondary electron mode (FE-SEM Tescan MAIA3) and semi-in-lens FE SEM JEOL JSM7500F microscope either with a cold cathode.

2.2.5. Contact angle measurement

The contact angles (surface free energy) of the samples surface were determined using the sessile drop method at room temperature. Three microliters of deionized water were separately dropped on each sample and captured by a digital USB camera. The contact angles (CA) were calculated by a multipoint fitting of the drop profile using Surface Energy Evaluation (SEE) software.

3. Results and discussion

Fig. 1 shows the top-view SEM images (upper row) and corresponding contact angles (bottom row) of the prepared samples. The bare SWCNT BP substrate (Fig. 1a) is composed exclusively from the CNTs bundles with only a small amount of impurities like residues of metal catalysts and other carbonaceous structures with a negligible effect on sample properties. In SWCNT BP/DNPs composite/heterostructure the DNPs form a homogeneous dispersion with SWCNTs (Fig. 1b). In contrast to these two samples, the diamond phases grown in/on the SWCNT BP/DNPs substrate almost creates a visible effect on sample properties. In SWCNT BP/DNPs composite/heterostructure the DNPs form a homogeneous dispersion with SWCNTs bundles with only a small amount of impurities like residues of metal catalysts and other carbonaceous structures with a negligible effect on sample properties.

The corresponding contact angles (CA) are shown in Fig. 1 (bottom row). The bare SWCNT BP exhibits a hydrophobic surface with a contact angle of 84°, which is in the range of typical CA values for BPs with entangled CNTs (70–110°) [28]. The CA of the SWCNT/DNPs sample is slightly lower (72°). This small difference is presumably caused by the presence of the DNPs in the SWCNT matrix. The DNPs are obtained by mechanical grinding of high-quality high-pressure high-temperature (HPHT) diamond microcrystals, which is known to form a hydrophilic surface [29]. On the other hand, significantly higher CA (126°) was observed for the NCD coated SWCNT BP (Fig. 1c). Here, the CA is influenced by the diamond film grown from hydrogen-rich plasma and by the increased surface roughness of the sample [30].

Fig. 2 compares Raman spectra of the bare SWCNT BP and the NCD coated BP substrate measured by four different laser excitation wavelengths (325, 442, 633 and 785 nm i.e. photon energies 3.815, 2.805, 1.959 and 1.579 eV) with a low laser power (10% of the total laser power – see subsection 2.2.1.). The observed Raman peaks/bands are summarized in Table 1. The Raman spectra of the SWCNT/DNPs composite are not shown being very similar to the bare SWCNT BP sample. In the case of the bare SWCNT BP (Fig. 2a), obvious differences observed in the Raman spectra measured with different wavelengths originate in a selective resonance of carbon nanotubes. The BP is composed of carbon nanotubes with different chiralities, diameters and with different allowed optical transitions. In other words, the Raman spectrum predominantly shows a signal from SWCNTs having the electronic transition in resonance with the laser excitation energy [31–34]. In the range of radial breathing mode (RBM), <500 cm<sup>-1</sup>, the peaks at 196 cm<sup>-1</sup> in the spectrum obtained with 442 nm laser excitation and at 206 cm<sup>-1</sup> with the 785 nm laser excitation represent the signals from semiconducting species in the diameter range from 1.2 to 1.3 nm [35]. The peak at 199 cm<sup>-1</sup> with 633 nm laser excitation originates from metallic tubes with a diameter of ~1.3 nm. In the spectrum obtained with the 325 nm laser excitation, no RBM peak was detected.

Fig. 2b shows Raman spectra of the SWCNT BP/NCDs measured by four different laser excitation wavelengths (325, 442, 633 and 785 nm). The obtained spectra do not reveal any characteristic peaks/bands outside the region 1000–2000 cm<sup>-1</sup>. Clearly, the spectra for the SWCNT BP/NCD samples are significantly different from those in Fig. 2a and moreover, the shape of the peaks and baseline strongly depend on the excitation wavelength. At 325 nm, a sharp and intensive diamond line (~1330 cm<sup>-1</sup>) and a broad band around 1600 cm<sup>-1</sup> are visible. At this wavelength, the NCD film is strongly absorbing [36]. Also, the sp<sup>3</sup> hybridized carbon bonds have higher Raman scattering efficiency at shorter excitation wavelengths. Thus, only the spectrum with the 325 nm laser excitation shows the sharp diamond line [37,38]. The broad band (~1600 cm<sup>-1</sup>) is attributed to sp<sup>2</sup> bonded carbon most probably localized at grain boundaries of diamond nanocrystals [39,40].

![Fig. 1. SEM images and corresponding contact angle measurements of a) bare SWCNT BP, b) SWCNT BP mixed with DNPs, c) SWCNT BP mixed with DNPs after CVD diamond growth (inset: detail on the grown diamond phases inside the pores) and d) cross-section SEM image of the SWCNT BP/NCD sample. (A colour version of this figure can be viewed online.)](image-url)
At longer excitation wavelengths, the diamond line disappears from the spectrum completely. The spectra are dominated by two broad features recognized as the D- and G-bands of sp² hybridized carbon [41]. The D-band is dispersive and shifts towards lower energies with decreasing excitation photon energy. Weak bands at around 1150 and 1450 cm⁻¹ are depicted in the spectra measured with 633 and 785 nm lasers excitation wavelengths (Fig. 1c). These bands are attributed to trans-polyacetylene chains at grain boundaries [23].

The spectra also exhibit strong baselines which come from photoluminescence (PL). In the spectrum acquired with 442 nm laser, a broad PL baseline increases with wavenumber whereas it decreases with wavenumber in the spectrum acquired with the 785 nm excitation wavelength. The broad PL baseline was also observed in the sp³ hybridized hydrogenated amorphous carbons [42]. Consequently, the Raman signal from the CNTs cannot be clearly recognized in the spectra primarily due to the NCD film absorption in the visible range.

The NCD film coverage, which suppresses the Raman features from CNTs can be modified/removed by an irradiation of higher power laser. Fig. 3 shows Raman spectra of the SWCNT BP/NCD sample measured with a different power $P_{exc}$ (5, 50 and 100% of the total laser power).
total laser power of 8.25 mW)) of a 442 nm laser. The Raman spectra accumulated with different laser powers (Fig. 3 - from bottom to up) were obtained from the same sample area. The Raman features noticeably alter depending on the used laser power. Increasing the laser power leads to significant changes in the spectrum. At 50% of the full laser power, i) the D broad band disappears, ii) the G band splits and iii) 2D band develops. In addition, the RBM peak is also seen below 200 cm⁻¹. The diamond peak at ~1330 cm⁻¹ is still visible which is superimposed over the broad and weak a-line, although it is hardly resolvable. At 100% of the laser power, i) the RBM peak at ~200 cm⁻¹ and the diamond peak at ~1330 cm⁻¹ almost disappear and ii) the 2D line is blueshifted. All these changes are irreversible as sequential decrease of the laser down to 5% (Fig. 3).

Clearly, the laser power density (which is in order of MW cm⁻²) at 50% level is high enough to damage and/or burn out a substantial part of the NCD layer. This process is completed when the laser operates at full power. Manifestation of a strong heating is also seen in the Raman lines of CNTs. It is known that the small diameter nanotubes can be burnt off by the Raman laser irradiation [43]. This can also be seen in our Raman RBM data. The up to 100% of laser power indicates that the RBM peak at ~200 cm⁻¹ disappears. The RBM peak is presumably redshifted and hidden below the cut off frequency ~170 cm⁻¹. Due to the 1/d (d is the nanotube diameter) dependence of the RBM frequency the redshift of the RBM corresponds to the larger mean diameter of CNTs. This can also be proven by the blueshift of the 2D line [44]. The G band in the spectrum taken at 50% laser power is relatively broad with two overlapping components. The band gets narrower and the components are better resolved when the spectrum is excited with the full laser power. This may be because the high power irradiation not only increases the mean diameter but also reduces the diameter distribution of nanotubes in the sample [43,45].

FTIR spectra of the different carbon forms are shown in Fig. 4. Firstly, we discuss the results acquired by a thin ATR prism (~25 internal reflections). The measured IR spectrum of pristine individual SWCNTs (Fig. 4a black curve) is dominated by a wide band centred at 5646 cm⁻¹ which is related to the excitonic optical transition at 0.7 eV of semiconducting SWCNTs [46]. The inset graph shows the detailed view of the 1000–2000 cm⁻¹ region. The peak at 1709 cm⁻¹ corresponds to the C=O stretching vibration in a carboxylic acid and lactones groups [47]. The peak at 1612 cm⁻¹ is related to a C=C stretching vibration originating from sp² hybridized carbon and a broad band between 1300 and 1100 cm⁻¹ is assigned as the C—O stretching vibration. The spectrum noticeably exhibits an onset of Drude absorption at the low frequency range associated with free-carriers in the metallic CNTs [48]. This finding well correlates with the Raman measurements showing a broad shoulder originated from the metallic CNTs when excited with the 633 nm laser (Fig. 2a).

The spectrum of pristine DNPs (Fig. 4a red curve) is dominated by the oxygen containing functional groups. The peak at 1770 cm⁻¹ is assigned as the C=O stretching vibration. The overlapping bands centred at 1000–1300 cm⁻¹ are related to C—O—C groups. The band at 1630 cm⁻¹ is most probably related to a C=C stretching vibration from sp² hybridized carbon. The IR spectra of SWCNT BP, SWCNT BP/DNPs and SWCNT BP/NCD samples are identical revealing the Drude absorption only and no other spectral features can be recognized (Fig. 4a).

On the other hand, with a thick ATR prism many absorption bands are observed in the IR spectra, as shown in Fig. 4b. Again, there is no difference observed between the spectrum of SWCNT BP and that of SWCNT mixed with DNPs. The two spectra from the SWCNT BP/DNPs and SWCNT BP/NCD show very similar features in two spectral ranges ~ above ~2800 cm⁻¹ and below ~1200 cm⁻¹. The dominant absorption in the 2800–3000 cm⁻¹ region is an indicative sign of the C—H symmetric and asymmetric stretching of CH₂ and CH₃ groups. The broad band centred at about 3300 cm⁻¹ corresponds to the O—H stretching of hydroxyl groups which originate from a carboxylic acid and/or water physically adsorbed on the sample surface. On the opposite side of the spectral range, the peaks at 869 and 956 cm⁻¹ correspond to C—H bending vibration of sp² hybridized bonding. The bands between 1000 and 1200 cm⁻¹ and at 1259 cm⁻¹ are assigned as the C—O stretching vibration [49,50].

In the middle part, absorption peaks due to sp² hybridized bonds dominate the spectrum of the SWCNT/DNPs sample. The band at 1412 cm⁻¹ corresponds to C—H bending or to O—H bending from a carboxylic acid. Well resolved peaks at 1541, 1579, and 1647 cm⁻¹ correspond to the stretching modes of the sp² hybridized C=C=C bonds that form the CNT backbone [51]. The absorption at 1757 cm⁻¹ is attributed to the stretching of the C=O bonds most probably from the carboxylic acid. In addition to these, peaks characteristic for the sp³ hybridization are recognized in the
spectrum of the SWCNT BP/NCD sample (Fig. 4b—blue curve). In particular, bending vibrations of sp3 hybridized CH2 and CH3 are well detectable at 1455 and 1366 cm−1, respectively. The peak at 1315 cm−1 is related to a C–C stretching vibration of the diamond crystal lattice [52–54].

Fig. 5 shows the deconvoluted high resolution C 1s XPS spectra of SWCNT BP filtrated without or with DNPs and after the CVD diamond growth (SWCNT BP/NCD). The calibration of C 1s peak of reference SWCNT BP and SWCNT BP/DNPs was made on 284.6 eV referenced to the sp2 carbon phase. The deconvolution of the C 1s peak of mentioned samples was complicated by the presence of the π–π* shake-up feature [55]. Therefore, the C 1s peaks were fitted with 5 peaks: sp2 (284.6 eV), sp3 (285.2 eV), C–O (286.8 eV) [56], C=O (288.9 eV) [57] and π–π* shake-up feature (291.0 eV). In the case of SWCNT BP/NCD, the C 1s peak was calibrated on 285.1 eV, which corresponds to the sp3 carbon phase. The deconvolution of the C 1s peaks of SWCNT BP/NCD was made into 4 different peaks: sp2 (284.2 eV), sp3 (285.1 eV), C–O (286.1 eV) and C=O (287.6 eV) [58].

Table 2 summarizes results (concentration of chemical elements and bonds as well as calculated sp3/sp2 ratio) evaluated from XPS measurements. The traces of nitrogen (2 and 1%) were observed in XPS spectra of SWCNT BP and SWCNT BP/DNPs samples, respectively. The detected nitrogen may originate from the remains of used surfactant (n-methyl pyrrolidone). The surprisingly high amount of oxygen in the SWCNT BP and the SWCNT BP/DNPs samples in comparison to the SWCNT/NCD sample can be explained by bonding of O (also contained in surfactant) to the uncompleted/defected carbon bonds on the CNTs fractions during the drying process. The increase of carbon and decrease of oxygen (oxygen bonds) was observed after the formation of carbon heterostructure and/or composite, i.e. adding of DNPs or the diamond growth.

The most pronounced changes in chemical composition between SWCNT BP and SWCNT BP/NCD are: decrease of oxygen (from 20 to 4%), increase of carbon concentration (from 78 to 96%) and absence of the nitrogen. These changes in the chemical composition significantly influence the C 1s peak deconvolution which shows a rapid increase of sp3 phase and a steep decrease of sp2 and oxygen bonds concentration. In addition, it could be also seen that the signal of π–π* shake-up feature totally disappeared in the SWCNT BP/NCD sample. This observation indicates the formation of a thick enough diamond film on the top of the BP substrate. The observed decrease of the oxygen concentration and/or hydrophilic functional groups as carbonyls on the sample surface after the diamond growth leads to a super-hydrophobic property. Thus the obtained XPS results/trends (chemical composition and bonds) can be correlated with the contact angle measurements (Fig. 1) showing a comparable wettability for the SWCNT BP and SWCNT BP/DNPs samples and a significant increase of the CA in the case of the SWCNT BP/NCD. In contrast to Raman and FTIR measurements these results also confirm, that XPS can easily detect the presence of a small amount of the DNPs incorporated to the SWCNT BP.

4. Conclusions

In this work we focused on the multiply spectroscopic characterization of the surface and near-surface region of the free-
standing single-wall carbon nanotubes buckypaper (BP) in its bare form, BP mixed with the diamond nanoparticles (DNPs) and BP coated by the nanocrystalline diamond film. Contact angle (CA) measurements confirmed a highly hydrophobic surface character for all of the samples. The super-hydrophobic property of SWCNT BP/NCD was attributed to hydrogen-rich plasma environment during the CVD diamond growth and the consequent decrease of the oxygen-based functional groups confirmed by XPS measurements. The CA features well correlate with the obtained XPS results in terms of the concentration of chemical elements and bonds as well as the calculated sp²/sp³ ratio on the substrates surface.

On the other hand, Raman and FTIR measurements revealed a complicated chemical structure in the near-surface region for which a careful choice of the experimental conditions is crucial. Raman measurements well recognized differences between sp² and sp³ hybridizations when appropriate laser intensity and laser excitation wavelength (i.e. considering the wavelength dependence Raman scattering efficiency of sp² and sp³ hybridized carbon bonds) was chosen. Increasing the laser power above a certain threshold level caused the damaging of NCD layer and NCD/CNT interface and changed the diameter distribution of nanotubes present in the buckypaper.

For FTIR measurements the used ATR prism thickness and/or the optical pathway length are important parameters. Due to a low threshold level caused the damaging of NCD layer and NCD/CNT system, a careful choice of the experimental conditions is crucial. The near-surface chemical composition, concentration of chemical bonds and sp³/sp² ratio on the samples surface calculated from XPS spectra.

Table 2

<table>
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<th>Sample</th>
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<td>N (at.%)</td>
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