N-doping and oxidation of carbon nanotubes and jellyfish-like graphene nanoflakes through the prism of Raman spectroscopy

Chernyak, Sergei A.; Ivanov, Anton S.; Stolbov, Dmitrii N.; Egorova, Tolganay B.; Maslakov, Konstantin I.; Shen, Zexiang; Lunin, Valery V.; Savilov, Serguei V.

2019

Chernyak, S. A., Ivanov, A. S., Stolbov, D. N., Egorova, T. B., Maslakov, K. I., Shen, Z., Lunin, V. V. & Savilov, S. V. (2019). N-doping and oxidation of carbon nanotubes and jellyfish-like graphene nanoflakes through the prism of Raman spectroscopy. *Applied Surface Science*, 488, 51-60. <https://dx.doi.org/10.1016/j.apsusc.2019.05.243>

<https://hdl.handle.net/10356/150610>

<https://doi.org/10.1016/j.apsusc.2019.05.243>

© 2019 Elsevier B.V. All rights reserved. This paper was published in *Applied Surface Science* and is made available with permission of Elsevier B.V.

Downloaded on 26 Apr 2023 11:08:54 SGT

N-doping and oxidation of carbon nanotubes and jellyfish-like graphene nanoflakes through the prism of Raman spectroscopy

Sergei A. Chernyak^{a}, Anton S. Ivanov^a, Dmitrii N. Stolbov^{a,b}, Tolganay B. Egorova^a,
Konstantin I. Maslakov^a, Zexiang Shen^c, Valery V. Lunin^a, Serguei V. Savilov^a*

^a Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1–3, Moscow,
119991, Russia

^b Ivanovo State University, Nanomaterials Research Institute, Ermak str., 37/7, 153025, Ivanovo,
Russia

^c Division of Physics and Applied Physics, School of Physical and Mathematical Sciences,
Nanyang Technological University, Singapore 637371, Singapore

* Corresponding author. E-mail: chernyak.msu@gmail.com

Present work demonstrates the differences between the structure and surface transformations of carbon nanotubes (CNTs) and graphene nanoflakes with small particle size (GNFs) under oxidation and N-doping using Raman spectra processing. Jellyfish-like GNFs are rather new material that differs from the commonly known graphene nanoflakes by rounded edges and small size of particles (less than 50 nm). This material is promising in electrochemistry due to its high specific capacitance. It was found that, despite the graphene nature of both CNTs and GNFs, their Raman spectra change differently under oxidation and N-doping because of the different growth mechanisms of CNTs and GNFs, strong curvature of carbon layers in CNTs, and a large number of edge carbon atoms in GNFs.

Keywords: carbon nanotubes; graphene nanoflakes; Raman spectroscopy; oxidation; N-doping

1. Introduction

Structured carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene are promising or have proven to be successful for use in composites, microelectronics, energy storage devices, sensors, catalysts and biomedicine [1, 2]. Some of these applications require structural or surface modification of carbon nanomaterials. For example, preparation of polymer composites with CNTs or their surface decoration with metal nanoparticles includes functionalization of the CNT surface usually achieved by oxidative treatment [3, 4]. The electronic properties of CNTs or graphene materials can be tuned by heterosubstitution of carbon atoms [5, 6]: nitrogen, boron, sulfur, and silicon atoms can be introduced in graphene sheets to change both the surface and bulk properties of the material [7, 8]. Nitrogen is the most popular dopant for CNTs and graphene because the size of N atoms is close to that of C ones whereas N-containing precursors are cheap and safe to use, and the synthesized materials are stable in air. Doped carbon nanomaterials show the promising properties in energy storage, electro- and heterogeneous catalysis, sensing devices, and fuel cells [9, 10].

Graphite exfoliation produces graphene nanoflakes or nanosheets with the domain size from hundreds of nanometers to microns [11-13]. These materials are usually studied for electrochemical [14], opto-electronic [15], and catalytic [16] applications. At the same time, N-doped small-size GNFs less than 50 nm in diameter obtained directly by hydrocarbon pyrolysis [17, 18] showed the promising properties in the electrode material of supercapacitors [19]. The main benefit of this synthesis technique is that GNFs with rather narrow size distribution and low stacking number of graphene layers can be synthesized in one stage and their purification does not require using sulfuric acid and potassium permanganate. The edges of these GNFs are rounded, so their shape resembles jellyfish [17].

Raman spectroscopy is a widely used technique to study graphene-based materials [20, 21]. It allows revealing their structure, the degree of graphitization, the presence of defects and amorphous impurities, etc [22-24]. In 1970 Tuinstra and Koenig published Raman spectroscopy study of graphite and

postulated that a single crystal produces only one Raman band at $\sim 1575\text{ cm}^{-1}$ attributed to E_{2g} stretching vibrations of graphite lattice of the infinite crystal [25]. Another band appeared at 1355 cm^{-1} in the Raman spectrum of polycrystalline graphite is associated with the A_{1g} mode of the lattice [26]. This band was established to originate not from the disordered carbon but from small crystallites or boundaries of large crystals. Later it was shown that the D band originates from the double resonant process [27, 28] and appears in Raman spectra of structured nanocarbons when the symmetry of the graphite unit cell is broken by an edge atom or heteroatom [29, 30]. These two bands were named as G and D band, respectively. The I_D/I_G intensity ratio is usually used as a parameter of the defectiveness of the carbon material [31]. The 2D (G') band observed in Raman spectra of graphitic materials at $\sim 2700\text{ cm}^{-1}$ results from a second-order two-phonon process, that is, this band is the D band overtone [32]. The 2G band is always observed in the spectra because it originates from a process where the momentum conservation is satisfied by two phonons with the opposite wave vectors; therefore no defects are required for the phonons activation [22]. Parameters of the Raman spectrum of a graphitic material correlate with its defectiveness that depends both on the synthesis conditions and further treatment (oxidation, functionalization, annealing, etc.). But usually only the I_D/I_G and $I_{G'}/I_G$ ratios are considered as indicators of the defectiveness of carbon material though much more information could be extracted from the spectra [23, 33-38]. However, because a plenty of carbon materials show similar Raman spectra, these spectra cannot be unambiguously interpreted and other techniques, such as TEM, XPS, XRD, etc. are required to draw clear conclusions.

This study is devoted to the comparative Raman spectroscopy analysis of two types of materials constructed from graphene planes: multi-walled CNTs, small-size few-layer graphene nanoflakes (GNFs), and their N-doped and oxidized derivatives. Though nanoparticles of both materials consist of several graphene layers, CNTs are 1D material, while GNFs can be attributed to “quazi-2D” one. The Raman spectra of CNTs and GNFs show many differences. Moreover, diverse location and orientation of

graphene layers lead to a significant contrast in the transformations of Raman spectra under N-doping and oxidative treatment.

2. Experimental

2.1. Preparation of materials

Multi-walled CNTs and N-CNTs were synthesized by the pyrolysis of hexane or acetonitrile over the Co-Mo/MgO catalyst in a quartz tubular reactor at 750°C. The synthesis details may be found in [39] for CNTs and in [34] for N-CNTs. In brief, nitrogen, bubbled through hexane or acetonitrile, was passed for 5 h over the catalyst prepared from cobalt and magnesium nitrates and ammonium molybdate. GNFs and N-GNFs were produced by the pyrolysis of the hexane or acetonitrile precursors for 30 min over the MgO template in a quartz tubular reactor at 800°C under the flow of nitrogen bubbled through the precursor. The MgO template was obtained from magnesium oxalate. Further details of the GNFs and N-GNFs syntheses may be found in [17] and [40], respectively. All the synthesized materials were purified from the catalyst/template and amorphous impurities by refluxing in 18% HCl water solution for 4 h followed by washing with distilled water until neutral pH, drying at 130°C and annealing in air at 350°C for 1 h. The purified samples were named as “CNT”, “GNF”, “N-CNT”, and “N-GNF”. Coal was produced by pyrolysis of birch sawdust in N₂ flow at 430 °C in an oven heated tubular quartz reactor described elsewhere [41].

The CNT and GNF materials were oxidized by refluxing in concentrated HNO₃ water solution, washed with distilled water until neutral pH and dried at 110°C. Pristine and N-doped carbon materials show different behavior under oxidation because of the higher defectiveness of N-doped graphene layers. For example, it was previously demonstrated that the maximum oxygen content in undoped CNTs was achieved after 3–6 h of nitric acid treatment [42] while that in N-doped CNTs was observed at oxidation time of 0.5–1 h, with the nitrogen content being strongly decreased during further oxidation [34]. That is

why the different oxidation times were chosen for the undoped and N-doped materials: 3 and 1 h, respectively. The oxidized materials were named as “CNTox”, “GNFox”, “N-CNTox”, and “N-GNFox”.

2.2. Characterization

Raman spectra of the samples were registered using a LabRam HR800 UV (Horiba Jobin Yvon, Japan) microscope-spectrometer (5 mW argon laser excitation with 514.5 nm wavelength and 50× Olympus lens). At least four spectra were acquired for each sample (Fig.S1–S8). OriginLab software was used for curve fitting. The number of components was chosen according to the fitting model (see Section 3.2). During fitting the positions of the D3 and D4 bands were restricted in the ranges of 1500–1515 cm^{-1} and $<1300 \text{ cm}^{-1}$, respectively, while the FWHMs for all bands were not fixed.

The specific surface area of the materials was measured by low temperature nitrogen adsorption using a Quantachrome AUTOSORB-1C/MS/TPR gas sorption analyzer. Prior to analysis, samples were degassed at 250°C for 3 h under vacuum. X-ray diffraction (XRD) patterns were recorded in the 2θ range of 10° to 70° using a Stoe Stadi P instrument equipped with a Ni-filtered $\text{CuK}\alpha$ X-ray tube. The interlayer distances were calculated using Bragg’s law. The position and FWHM of the graphitic (002) reflection were obtained by curve fitting of the XRD diffraction pattern using the Pseudo-Voigt profile. The morphology and structure of the samples were studied using a JEOL 2100F/Cs transmission electron microscope (TEM). Electron diffraction patterns were registered using selected area electron diffraction (SAED). The oxygen and nitrogen contents in the samples were determined using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS) with a monochromatic Al $\text{K}\alpha$ source ($h\nu = 1486.7 \text{ eV}$, 150 W).

The BET specific surface area and the N and O contents in the samples are shown in Table 1.

Table 1. Specific surface area (S_{BET}), XPS oxygen and nitrogen contents and N/C and O/C atomic ratios in the studied samples.

Sample	S_{BET} (m^2/g)	Oxygen (at.%)	Nitrogen (at.%)	O/C	N/C
CNT [42]	192	0.3	0	0.003	0
N-CNT	270	1.5	1.6	0.015	0.017
CNTox [42]	233	8.0	0.8	0.088	0.009
N-CNTox	200	7.1	1.1	0.077	0.012
GNF	1495	0.7	0	0.007	0
N-GNF	1036	3.3	9.6	0.038	0.110
GNFox	54	17.0	0.9	0.207	0.011
N-GNFox	120	10.0	8.5	0.123	0.104

3. Results and discussion

3.1. General characterization of pristine CNTs and GNFs

Both CNTs and GNFs consist of several graphene sheets. In the case of CNTs these sheets are rolled up and very long in axial direction, whereas in GNFs they are flat, smaller (less than 50 nm) and bent at the edges. TEM images show more perfect layered structure and uniform interlayer spacing in the case of pristine CNTs compared to GNFs (Fig.1). The graphitic structure persists even at bends of CNTs. At the same time, the variation of interlayer distance is observed within GNFs as a result of the distortion of layers.

Fig.1. TEM images of pristine CNTs (a,b) and GNFs (c,d).

XRD data confirm the difference in the graphitization degree between pristine CNTs and GNFs (Fig.2). The graphite (002) peak is clearly seen in the XRD pattern of CNTs at 25.7° in contrast to the broad peak at $\sim 23.2^\circ$ in the semi-amorphous pattern of GNFs. XRD data correlate with SAED patterns in which the graphite (002) reflections are observed in the case of CNTs (Fig.1a) whereas only amorphous halo is seen for GNFs (Fig.1c). The small peaks in the XRD patterns of GNFs samples at $\sim 21.9^\circ$ and 31.4° can be attributed to the residual SiO_2 (PDF card #71-821) from the quartz reactor used for synthesis. The presence of the halo and the asymmetric tail at the left side of the (002) peak in the XRD pattern of pristine GNFs correspond to the scattering of the interlayer distance towards higher values which is consistent with the SAED signal blurring towards the center of the pattern (Fig.1c). Therefore, on the base of TEM and XRD results it can be concluded that the CNT structure is more perfect compared to GNF one.

Fig.2. XRD profiles of graphitic (002) peak and calculated interlayer distances in the studied samples.

The structural differences between GNFs and graphite result from the small particle size and great amount of edge carbon atoms in GNFs that lead to a disorder in the arrangement of graphene layers, that is, to the partially turbostratic structure of particles. The difference in the structure of CNTs and GNFs determines the difference between their Raman spectra. Indeed, the strong broadening of the D-band at $\sim 1350 \text{ cm}^{-1}$ in the Raman spectrum of GNFs makes it similar to that of soot and coal, while the spectrum of CNTs is close to that of polycrystalline graphite (Fig.3).

Fig.3. Raman spectra of GNFs, CNTs, and their oxidized and N-doped derivatives. Coal spectrum is also shown for comparison.

3.2. Curve fitting of Raman spectra

Accurate characterization of the studied materials by Raman spectroscopy requires careful choosing of both the set of analyzed bands and the fitting model. The Raman spectra of CNTs and GNFs differ both in the range of 800–2000 and 2000–3500 cm^{-1} (Fig.3). In this work we will predominantly consider the former region because the latter one contains overtones of the G and D bands, which complicates the analysis. The 800–2000 cm^{-1} region of the CNT spectrum can be fitted by five components [30, 33]. Besides the main D1 and G peaks that correspond to edge carbon atoms and E_{2g} stretching vibrations of graphite lattice, respectively, three additional defect related peaks (D2, D3 and D4) can be also identified. These peaks are usually assigned to amorphous fraction, fragments of surface

graphene layers of CNTs (D3 and D4), stacking defects (D3), and small-size graphene clusters (D2) [30, 33-35]. Fitting parameters, such as intensities, areas and widths of the peaks or their ratios, allow tracing the structure differences between the studied materials. The Raman spectrum parameters considered in this work and their explanation are presented in Table 2. Along with the intensity ratios of the Raman peaks (bands) that are widely used for characterizing carbon nanomaterials, curve fitting of Raman spectra also yields the areas of the peaks. In contrast to the intensity ratios, the area ratios can provide more reliable information because the possible broadening of the peaks is taken into account. In this work we traced both the intensity and area ratios of the Raman bands and found that all trends were quite similar but more pronounced changes were observed for the area ratios. In case of GNFs there was no opportunity to fit the second order region (G' band), therefore, only the $I_{G'}/I_G$ intensity ratio was available.

Table 2. Raman spectral parameters considered in the present work and their interpretation on the base of works [25, 30, 31, 33-35, 43-51]. S, I, and W are, respectively, the area, intensity, and FWHM of the Raman band.

Parameter	Relation to the graphitic material structure and defects
S_{D1}/S_G	Carbon atoms with broken symmetry of the graphite cell (near edges, defects or heteroatoms)
S_{D3}/S_G	Polyene-/polyphenylene-type fragments (amorphous carbon) or stacking defects
S_{D4}/S_G	Polyene-/polyphenylene-type fragments (amorphous carbon)
$I_{G'}/I_G$	Interlayer defects
$W(D1) \text{ (cm}^{-1}\text{)}$	Structuring degree of the amorphous fraction
$W(G) \text{ (cm}^{-1}\text{)}$	Structuring degree of the graphitic fraction
$S(G) \text{ (%)}$	The fraction of the intact non-defective graphitic clusters (G band area relative to the total area of the 800–2000 cm^{-1} region)

According to the literature the most suitable function for fitting the 800–2000 cm^{-1} region in the Raman spectrum of CNTs is Lorentzian for the D1, D2, D4, G bands and mixed Gaussian–Lorentzian for the D3 band [30, 33, 34] (Fig.4).

Fig.4. Curve fittings of the 800–2000 cm^{-1} region in the Raman spectra of CNTs and GNFs. Two different fitting models were used for the GNFs spectrum. L, G and PV denote Lorentzian, Gaussian, and Pseudo-Voigt profiles, correspondingly.

The D2 band cannot be reliably extracted from the Raman spectrum of GNFs (Fig.4), which was previously pointed in [52]. This band corresponds to the central ring breathing mode with surrounding asymmetric stretch behavior in small-sized graphene fragments according to Smith et al. [35] and originates from intravalley one- and two-phonon Raman processes, respectively, involving one longitudinal optical phonon near the Γ point and one defect [53]. In the spectrum of GNFs the G band shifts to higher wavenumbers overlapping with the D2 band. Such overlapping under disordering of graphitic materials was also observed in [54–56] and the 2D2 band was used as an evidence of the D2 band presence. In the present study second-order region contains a broad peak between ~ 2300 and ~ 3300

cm^{-1} that is difficult to fit due to the increased FWHMs of all components. The formation of the single G+D2 band in graphene oxide (GO) was also discussed in [53] as a result of the phonon quantum confinement effect induced by the small domain size in GO. Different fitting models may be applied to the Raman spectrum of GNFs, and we chose two sets of fitting functions depending on the way we consider this material (Fig.4).

- **Model I.** The D4, D1, and G bands are fitted with Lorentzian profiles, while the D3 band – with a Gaussian one, the same way as it was done for CNTs. In this model GNFs are considered as dispersed graphitic particles containing amorphous impurities (“top-down” approach). The difference between the application of this model to CNTs and GNFs is the presence of separate component for the D2 band in the former case.
- **Model II.** GNFs are treated as stacks of small diameter graphene clusters. If we accept the range of particle diameter of 10–50 nm and the largest diagonal of the benzene ring of 0.28 nm, the GNF diameter will correspond to a sequence of 36–179 benzene rings. In this case, we can use the curve fitting approach proposed for estimating the size of graphene fragments in coals [35]. In this approach the Gaussian profile was suggested for the D1, D3, and D4 bands while the mixed Lorentzian – Gaussian profile can be applied for the G band: smaller size of the graphene cluster leads to more Gaussian profile of the G band. In the present work we decided to use Pseudo-Voigt function for the fitting of the G band (Fig.4). The μ index in this function varies from 0 for the Gaussian profile to 1 for the Lorentzian one. Such an approach can be referred as “bottom-up” since GNF particles are considering not as a reduced graphite/graphene but as an “overgrown” coronene/ovalene/etc.

For a certain spectrum these different fitting models yield different sets of parameters that cannot be directly compared. Each model has its own advantages and disadvantages depending on the material nature and the objectives of the study. For example, in the case of pristine GNFs and their comparison

with other graphene-like materials (CNTs, graphene, and graphite) model I is more suitable because it makes possible to compare the intensity ratios of the D and G bands, their widths and positions in Raman spectra of different materials. At the same time, model II is more convenient for the comparison of pristine and doped GNFs (see chapter 3.4).

3.3. Results of curve fitting for undoped non-oxidized materials

The Raman spectra of all studied materials are presented in Fig.3. Fig.5 demonstrates the results of curve fitting of the CNT, GNF, CNTox, GNFox, N-CNT, and N-CNTox spectra using model I. The equation for the average in-plane crystallite size (L_a) of a nanostructured graphitic material proposed by Ribeiro-Soares et al. [52] can be applied to the GNF Raman spectrum fitted using model I (Lorentzian profile of the G band): $L_a = (l_c/2) * \ln[C/(W_G - W_G^\infty)]$, where l_c is the photon coherence length (~32 nm), C is the constant (95 cm^{-1}), W_G^∞ represents $W(G)$ for undoped pristine graphene (15 cm^{-1}). Another equation was proposed by Cançado et al. [57, 58]: $L_a \text{ (nm)} = 560/[W_G - 11]$. Both equations yield L_a for the pristine GNF sample in the range of 7–9 nm that is smaller than the particle size, which reflects the presence of defects inside graphene layers.

Fig.5. Results of curve fitting of the Raman spectra of CNTs and GNFs using model I (See section 3.2).

The results of curve fitting of the Raman spectra of pristine CNTs and GNFs indicate that CNTs are more structured material with higher degree of graphitization. Graphene layers in GNFs contain distortions of bond angles and lengths, which results in higher W(G), broader two-phonon bands, and lower S(G) for GNFs compared to CNTs despite the fact that graphene layers in CNTs are folded. Wider G band and higher S_{D3}/S_G , and S_{D4}/S_G ratios testify the significant amorphization of GNFs and layer bending in their structure. Lower $I_{G'}/I_G$ ratio in this case correlates with the deviation of the XRD interplanar distance from that of the ideal graphite structure. The significantly higher S_{D1}/S_G ratio for GNFs reflects the great number of edge carbon atoms. Similar Raman spectra were obtained in work [52] for the polycrystalline graphite samples with different in-plane crystallite size (L_a) of 3.8–17 nm.

Finally, it is worth noting that the G band in GNFs is strongly shifted towards higher wave numbers up to 1600 cm^{-1} . Its position is close to that of the D2 band corresponded to vibrations of central ring in polyaromatic fragments or small graphene clusters [35, 43] or graphene lattice vibrations involving only surface layers, and hence can represent the high surface-to-volume ratio [50, 59]. Thus, it can be proposed that some “averaged” G–D2 band is observed in the Raman spectrum of GNFs because of the small diameter and thickness of particles, which is consistent with work [55].

3.4. N-doping of CNTs and GNFs

N-doping of CNTs is known to result in the appearance of bamboo-like structure (Fig.6). The use of acetonitrile as a precursor in the CVD synthesis allowed introducing 2–3 at.% of nitrogen into CNTs (Table 1) and turn their cylindrical structure into bamboo-like one [34].

Fig.6. TEM images and SAED patterns of N-CNTs (a,b) and N-GNFs (c,d).

Though the Raman spectra of CNTs and N-CNTs are similar (Fig.3), curve fitting reveals some differences between these materials. The G band in N-CNTs is shifted to higher wave numbers (Fig.5d). Lower relative area of this band, higher S_{D3}/S_G , S_{D4}/S_G , and S_{D1}/S_G ratios and broader D1 band (Fig.5a,b,c) testify the slightly lower graphitization degree of N-CNTs compared to pristine CNTs.

These results along with the similar values (within the experimental error) of both the I_G/I_G ratio (Fig.5c) and the interplanar distance (Fig.2) for CNTs and N-CNTs demonstrate that doping with nitrogen adds extra curvatures and defect sites into the structure of CNTs but do not significantly affect their layered structure.

The Raman spectrum of N-doped GNFs, as well as the spectrum of pristine GNFs, is close to that of amorphous carbon and coal (Fig.3). The SAED patterns of GNFs and N-GNFs are also close (Fig.1c and 5c, respectively). Similar Raman spectra were obtained for large-size (300–500 nm) N-GNFs hydrothermally synthesized over MgO template [60]. Careful processing of the N-GNF Raman spectrum revealed that the “top-down” fitting approach (model I) was not applicable in this case (See the comparison between the model I and II curve fittings for the N-GNF sample in Fig.S9a,b). Therefore, this spectrum was analyzed using only the “bottom up” approach (model II) and the spectrum of pristine GNFs was processed the same way to correctly compare these materials. Such inapplicability of model I can be explained by the structure of N-GNFs in which polyaromatic graphene domains are separated by N atoms (see the discussion of Fig.8). It should be noted that model II cannot be used for N-CNTs because of the uncertainty of the D2 band position in the case of the Pseudo-Voight profile of the G-band (See the comparison between model I and II fittings with the D2 band component for N-GNT sample in Fig.S9c,d). Fig. 7 shows the results of curve fitting of the Raman spectra of GNFs and N-GNFs. The broadening of the D and G bands after N-doping of GNFs is clearly seen while the relative area of the G band does not change within the experimental error. N-doping leads to the distortion of the angles and lengths of C–C bonds in the aromatic ring, but at the same time it does not affect the overall graphitic structure and morphology of the particles. The latter statement is also proved by the XRD data (Fig.2) and the I_G/I_G ratio (Fig.7b): interlayer distance in N-GNFs is even smaller and slightly closer to that in graphite than to that in pristine GNFs; the I_G/I_G ratio for N-GNFs is higher than that for the undoped material. On the other hand, the concentration of defects in N-GNFs is higher compared to pristine GNFs. It was theoretically calculated that the N-doped graphenes with various doping levels can form an unusual

two-dimensional π - π bonding in a bilayer, bringing the neighboring N-doped graphenes to significantly reduced interlayer separations [61]. Moreover, this effect becomes more pronounced with the increase in the N content up to ~12–13 at.% that is close to that in the N-GNF sample. The S_{D4}/S_G ratio within the experimental error doesn't change after N-doping. The S_{D3}/S_G and S_{D1}/S_G ratios increase because of the amorphization of the material and breaking of graphitic lattice symmetry by heteroatoms (Fig.7b). It is worth noting that the average particle sizes of GNFs and N-GNFs are rather similar: 21.9 ± 0.9 and 23.6 ± 0.9 nm, respectively (according to TEM, see Fig.S10), therefore, the difference in the S_{D1}/S_G ratio originates from nitrogen doping rather from the size effect.

Fig.7. Results of curve fitting of the Raman spectra of GNFs using model II (See section 3.2).

The L_a cannot be calculated for N-GNFs because it is impossible to fit the G band with the Lorentzian profile. At the same time higher W(G) for this sample compared to pristine GNFs reflects the decrease of L_a as a result of the incorporation of N atoms into graphene layers. Interestingly, the growth of the S_{D1}/S_G ratio is not so sharp in contrast to that observed under N-doping of graphene [62]. This can be explained by the high initial concentration of defects in GNFs compared to graphene, which makes it difficult to reveal the N-doping effect. Summarizing the above presented results it can be concluded that

N-doping of GNFs at the pyrolysis stage introduces planar defects and slightly changes the layer structure.

Let's consider a graphene fragment containing 110 carbon atoms (42 rings) (Fig.8a). Typically, the nitrogen content in N-doped GNFs varies in the range of 9–12 at.% according to XPS and elemental analysis [63]. In the present study N-GNF sample contains 9.6 at.% of N (Table 1), which corresponds to the substitution in the considered fragment of about 10 carbon atoms with nitrogen ones. The resulted N-doped GNF fragment may be divided into undoped domains containing N atoms only on their boundaries (Fig.8b). It should be also taken into account that pyridine and pyrrole nitrogen species are also present in N-GNFs [40], which introduces additional edges at the domain boundaries (Fig.8c).

Fig.8. Graphene fragment in GNF before (a) and after N-doping (b,c) that introduces into this fragment only graphitic/quarternary (b) or graphitic/quarternary, pyrrolic, and pyridinic (c) nitrogen species. The undoped graphene domains confined by nitrogen atoms are shown in N-doped GNF fragments.

As it was discussed in Section 3.2, in the case of coals the possibility of G band fitting with a Lorentzian profile for large graphitic fragments and with a Gaussian one for nanodispersed graphene clusters was considered in [35]. As N-doping divides a graphene layer into smaller unsubstituted domains (polyaromatic fragments), the Pseudo-Voigt function may be applied to estimate the nitrogen content in

N-GNFs. The μ coefficient in this function represents the Gaussian–Lorentzian ratio and varies from 0 for the Gaussian to 1 for the Lorentzian profiles. We can assume that the decrease in the domain size changes the G band profile to more Gaussian, that is, μ is expected to decrease with N-doping of GNFs. Therefore, it may be possible to trace N-doping using the μ coefficient of the Pseudo-Voigt profile applied for fitting of the G band. Indeed, μ decreases after N-doping of GNFs (Fig. 9), which qualitatively proves the discussion above. At the same time, oxidation leads to the increase of μ , which correlates with the XRD and SAED data (Fig.3 and Fig.2c, Fig.6c, Fig.11a,d). Thus, the decrease of μ can be considered as a qualitative indicator of N-doping, that is, of amorphization of the material.

Fig.9. μ coefficient of Pseudo-Voigt profile of the G band in the Raman spectra of pristine, N-doped GNFs, and their oxidized derivatives. μ is equal to 1 for the Lorentzian and 0 for the Gaussian profiles.

3.5. Oxidation of CNTs and GNFs

CNT oxidation by nitric acid water solution was thoroughly studied in our previous work [33]. TEM images demonstrate cutting of nanotubes and destruction of the surface layers under oxidation (Fig.10 a-c).

Fig.10. TEM images of CNTox (a-c) and N-CNTox (d-f).

Several simultaneous processes occur during CNT oxidation, including complete oxidation of the amorphous fraction and thin or short CNTs, exfoliation of surface layers, cutting of long nanotubes, and opening of channels [33]. As a result, the increase in the number of edge carbon atoms and the appearance of fragments of the destroyed upper layers, on the one hand, and the structuring of material, on the other hand, lead to the changes in the Raman spectra of CNTs under oxidation (Fig.5a). During oxidation the impact of the defects introduced by amorphous particles and CNT bends is replaced by that of fragments of the destroyed upper layers. As a result, the most structured CNTs remain in the sample. Therefore, the total number of defects increases, but the widths of the D1 and G bands in the Raman spectrum decrease. For example, the width of the G band for the oxidized CNTs is close to that for graphite (less than 50 cm^{-1}). The slight up-shift of the G band also indicates the formation of exfoliated

fragments (Fig.5d). In other words, oxidized CNTs contain well-ordered nanotubes covered with the great number of exfoliated fragments.

N-doped CNTs are oxidized faster than pristine ones because of their higher defectiveness and curvature [34]. After nitric acid treatment the S_{D1}/S_G and S_{D3}/S_G ratios grow while the S_{D4}/S_G one doesn't change or even decreases (Fig.5b,c). The FWHMs of the G and D1 bands only slightly grow (in fact insignificantly within the experimental error) because several simultaneous processes, such as gradual oxidation of inner “bridges” (Fig.10e), destroying of surface layers (Fig.10f), cutting of nanotubes (Fig.10d), and gasification of the most amorphous fragments, take place during N-CNT oxidation. These processes seem to compensate each other. Actually, oxidation affects N-CNTs in a different way than the pristine CNTs: the interlayer distance and the G band position in N-CNT grow while the $W(G)$ parameter of their Raman spectrum remains unchanged (Fig.5a).

Oxidation of both undoped and N-doped GNFs leads to the similar changes in their structure. In this case in contrast to CNTs and N-CNTs the slight reduction in the number of stacking defects and those responsible for the fragments of the destroyed surface layers is observed (Fig.7b). We assume that the edges of both pristine and N-doped GNFs are bent and highly-defective. The nanoflakes in their turn are randomly oriented to each other forming a low-density material. Two important processes occur during oxidation: removal of the most amorphous or the smallest GNFs and the formation of dense macro-particles in which nanoflakes are packed because of the high degree of their functionalization and the affinity of functional groups to each other. The second process can be better illustrated by the sharp decrease in the S_{BET} after acid treatment (Table 1). The total number of edge carbon atoms is unchanged because oxidation mainly proceeds at edges rather than in planes. The overall structuring of both GNFs and N-GNFs after oxidation is also confirmed by their electron diffraction patterns (Fig.2, Fig.11a, and Fig.11d). At the same time, SAED shows slightly stronger amorphization of oxidized N-GNFs compared to GNFs (see the continuous halo in the center of the diffraction pattern in Fig.11d). Raman data also demonstrate a noticeable difference between the N-GNFox and GNFox samples: the spectrum of the

former one shows higher S_{D1}/S_G ratio and broader D1 and G bands. The interlayer distance in N-GNFox calculated from XRD was closer to that in graphite than the interlayer distance in GNFox while the electron diffraction patterns show the appearance of (101) graphitic ring in both cases but with more amorphous halo for N-GNFs (Fig.11a,d).

Fig.11. TEM images and SAED patterns of GNFox (a-c) and N-GNFox (d-e) samples. Arrows indicate the sites where the noticeable changes are observed after oxidation.

Thus, it can be summarized that the oxidation of CNTs and N-CNTs occurs in a slightly different way, while GNFs and N-GNFs show similar changes under this treatment.

Conclusions

The changes in the structure of carbon nanotubes and small-size jellyfish-like graphene nanoflakes under N-doping and oxidation have been studied by Raman spectroscopy. Low size of graphene

nanoflakes, their turbostratic orientation, and great amount of edge carbon atoms in GNFs determine their amorphous-like Raman spectra with the strong broadening of the D1 and G bands. Two different models were applied for curve fitting of the 800–2000 cm^{-1} region in the Raman spectra of GNFs based materials. In these models GNFs are considered as a highly dispersed graphene/graphite or as an “overgrown” coronene/ovalene/etc. Both models imply four Raman bands: D1, D3, D4, and G. The G band in GNFs is noticeably shifted towards higher wavenumbers compared to CNTs because of the small size of graphene domains.

N-doping of CNTs and GNFs does not significantly affect their layered structure but introduces a lot of defects into the layer: it changes bond angles and lengths and forms holes and new edges within layers. This results in the increase in the relative intensities of all disordered components in the Raman spectra. The most significant difference in the N-doping of CNTs and GNFs is that the heterosubstitution changes the CNT structure at the growth stage and introduces additional curvatures into nanotubes, while in the case of GNFs nitrogen doping produces only planar defects. In addition, great amount of nitrogen increases the interaction between particles and graphene layers of GNFs, which reduces the interlayer distance and slightly decreases the I_G/I_D ratio because of the elimination of interlayer defects. The Pseudo-Voigt profile of the G band was found to be sensitive to N-doping: the Lorentzian profile of the G band in GNFs changes to the mixed Gaussian–Lorentzian one after doping, while the opposite trend was observed after oxidation.

Oxidation occurs differently for CNTs and N-CNTs, while it demonstrates similarity for GNFs and N-GNFs. Though the graphitic structure of CNTs becomes more perfect under the acid treatment because of removal of the most curved and defect nanotubes, the overall concentration of intact graphitic clusters decreases. At the same time, in the case of GNFs, the noticeable graphitization takes place because of the significant reduction in the number of stacking and interlayer defects and those responsible for the fragmentation of surface layers. The important factor here is the compaction and densification of the material and the disappearance of the turbostratic particle orientation. The oxidation of N-CNTs

differs from that of undoped CNTs: the interlayer distance grows while the $W(G)$ parameter of the Raman spectrum does not change because of the inherent bamboo-like structure of N-CNT walls. Thus, in general, the difference between the oxidation of CNTs and GNFs can be explained as follows. In CNTs the oxidation leads to the destruction of surface layers and cutting of nanotubes. This results in the growth of the number of edge carbon atoms and defect fragments and, hence, the S_{D1}/S_G , S_{D3}/S_G , and S_{D4}/S_G ratios increase. Oxidation of GNFs seems to only remove the most amorphous particles, while the average size of GNFs and the number of the edge carbon atoms remains unchanged. As a result, the S_{D1}/S_G , S_{D3}/S_G , and S_{D4}/S_G ratios for oxidized GNFs and CNTs are close to each other.

The results of this work should be useful for the study of 1D and 2D graphene-based materials, and not only by Raman spectroscopy. Fitting model I as it is used in this work or with the additional component attributed to the D2 band can be applied to any graphitic-based material while model II is more suitable for amorphous carbons and highly-dispersed graphenes/graphites.

Acknowledgments

The authors thank Dr. O.Y. Isaikina for Raman spectroscopy study and Dr. A.V. Egorov for his help in TEM investigations. This work was supported by the Russian Science Foundation under grant No. 18-13-00217. The authors acknowledge support from "Nanochemistry and Nanomaterials" MSU Equipment Center acting under Lomonosov Moscow State University Program of Development.

References

- [1] M.F.L. De Volder, S.H. Tawfick, R.H. Baughman, J. Hart, Carbon Nanotubes: Present and Future Commercial Applications, *Science*, 339 (2013) 535-539.
- [2] Y. Zhu, H. Ji, H.-M. Cheng, R.S. Ruoff, Mass production and industrial applications of graphene materials, *National Science Review*, 5 (2018) 90-101.
- [3] N.G. Sahoo, S. Rana, J.W. Cho, L. Li, S.H. Chan, Polymer Nanocomposites Based on Functionalized Carbon Nanotubes, *Prog. Polym. Sci.*, 35 (2010) 837-867.

- [4] H. Xiong, L.L. Jewell, N.J. Coville, Shaped Carbons As Supports for the Catalytic Conversion of Syngas to Clean Fuels, *ACS Catalysis*, 5 (2015) 2640-2658.
- [5] Q. Liu, J. Zhong, Z. Sun, H. Mi, Cross-linked carbon networks constructed from N-doped nanosheets with enhanced performance for supercapacitors, *Appl. Surf. Sci.*, 396 (2017) 1326-1334.
- [6] J. Palomino, D. Varshney, B.R. Weiner, G. Morell, Study of the Structural Changes Undergone by Hybrid Nanostructured Si-CNTs Employed as an Anode Material in a Rechargeable Lithium-Ion Battery, *J. Phys. Chem. C*, 119 (2015) 21125-21134.
- [7] M. Hu, Z. Yao, X. Wang, Graphene-Based Nanomaterials for Catalysis, *Ind. Eng. Chem. Res.*, 56 (2017) 3477-3502.
- [8] W. Qian, X. Cui, R. Hao, Y. Hou, Z. Zhang, Facile Preparation of Nitrogen-Doped Few-Layer Graphene via Supercritical Reaction, *ACS Appl. Mater. Interfaces*, 3 (2011) 2259-2264.
- [9] M. Inagaki, M. Toyoda, Y. Soneda, T. Morishita, Nitrogen-doped carbon materials, *Carbon*, 132 (2018) 104-140.
- [10] Y. Fengkai, X. Wei, M. Artjom, M. Justus, H. Dirk, S. Ilya, et al., NH₃ Post-Treatment Induces High Activity of Co-Based Electrocatalysts Supported on Carbon Nanotubes for the Oxygen Evolution Reaction, *ChemElectroChem*, 4 (2017) 2091-2098.
- [11] H. Han, Y. Zhang, N. Wang, M.K. Samani, Y. Ni, Z.Y. Mijbil, et al., Functionalization mediates heat transport in graphene nanoflakes, *Nat. Commun.*, 7 (2016) 11281.
- [12] M. Kumar, B.E.K. Swamy, M.H.M. Asif, C.C. Viswanath, Preparation of alanine and tyrosine functionalized graphene oxide nanoflakes and their modified carbon paste electrodes for the determination of dopamine, *Appl. Surf. Sci.*, 399 (2017) 411-419.
- [13] V. Castagnola, W. Zhao, L. Boselli, M.C. Lo Giudice, F. Meder, E. Polo, et al., Biological recognition of graphene nanoflakes, *Nat. Commun.*, 9 (2018) 1577.

- [14] X. Li, K. Zhou, J. Zhou, J. Shen, M. Ye, CuS nanoplatelets arrays grown on graphene nanosheets as advanced electrode materials for supercapacitor applications, *Journal of Materials Science & Technology*, 34 (2018) 2342-2349.
- [15] S. Sanyal, A.K. Manna, S.K. Pati, BN-decorated graphene nanoflakes with tunable opto-electronic and charge transport properties, *J. Mater. Chem. C*, 2 (2014) 2918-2928.
- [16] J.-L. Meunier, N.-Y. Mendoza-Gonzalez, R. Pristavita, D. Binny, D. Berk, Two-Dimensional Geometry Control of Graphene Nanoflakes Produced by Thermal Plasma for Catalyst Applications, *Plasma Chem. Plasma Process.*, 34 (2014) 505-521.
- [17] S.A. Chernyak, A.M. Podgornova, E.A. Arkhipova, R.O. Novotortsev, T.B. Egorova, A.S. Ivanov, et al., Jellyfish-like few-layer graphene nanoflakes: Synthesis, oxidation, and hydrothermal N-doping, *Appl. Surf. Sci.*, 439 (2018) 371-373.
- [18] S.A. Chernyak, D.N. Stolbov, A.S. Ivanov, S.V. Klovov, T.B. Egorova, K.I. Maslakov, et al., Effect of type and localization of nitrogen in graphene nanoflake support on structure and catalytic performance of Co-based Fischer-Tropsch catalysts, *Catal. Today*, (2019).
- [19] E.A. Arkhipova, A.S. Ivanov, S.V. Savilov, K.I. Maslakov, S.A. Chernyak, Y.A. Tambovtseva, et al., Effect of nitrogen doping of graphene nanoflakes on their efficiency in supercapacitor applications, *Functional Materials Letters*, 11 (2018) 1840005.
- [20] A. Merlen, J. Buijnsters, C. Pardanaud, A Guide to and Review of the Use of Multiwavelength Raman Spectroscopy for Characterizing Defective Aromatic Carbon Solids: from Graphene to Amorphous Carbons, *Coatings*, 7 (2017) 153.
- [21] Y. Jiang, J. Wang, L. Malfatti, D. Carboni, N. Senes, P. Innocenzi, Highly durable graphene-mediated surface enhanced Raman scattering (G-SERS) nanocomposites for molecular detection, *Appl. Surf. Sci.*, 450 (2018) 451-460.
- [22] A.C. Ferrari, D.M. Basko, Raman spectroscopy as a versatile tool for studying the properties of graphene, *Nat Nano*, 8 (2013) 235-246.

- [23] S.L.H. Rebelo, A. Guedes, M.E. Szeftczyk, A.M. Pereira, J.P. Araujo, C. Freire, Progress in the Raman spectra analysis of covalently functionalized multiwalled carbon nanotubes: unraveling disorder in graphitic materials, *Phys. Chem. Chem. Phys.*, 18 (2016) 12784-12796.
- [24] M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, L.G. Cancado, A. Jorio, R. Saito, Studying disorder in graphite-based systems by Raman spectroscopy, *Phys. Chem. Chem. Phys.*, 9 (2007) 1276-1290.
- [25] F. Tuinstra, J.L. Koenig, Raman Spectrum of Graphite, *The Journal of Chemical Physics*, 53 (1970) 1126-1130.
- [26] E. Kusiak-Nejman, R.J. Wróbel, J. Kapica-Kozar, A. Wanag, K. Szymańska, E. Mijowska, et al., Hybrid carbon-TiO₂ spheres: Investigation of structure, morphology and spectroscopic studies, *Appl. Surf. Sci.*, (2018).
- [27] C. Thomsen, S. Reich, Double Resonant Raman Scattering in Graphite, *Phys. Rev. Lett.*, 85 (2000) 5214-5217.
- [28] C. Thomsen, S. Reich, Raman Scattering in Carbon Nanotubes, in: M. Cardona, R. Merlin (Eds.) *Light Scattering in Solid IX*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2007, pp. 115-234.
- [29] Y. Wang, D.C. Alsmeyer, R.L. McCreery, Raman spectroscopy of carbon materials: structural basis of observed spectra, *Chem. Mater.*, 2 (1990) 557-563.
- [30] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Pöschl, Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information, *Carbon*, 43 (2005) 1731-1742.
- [31] S. Osswald, M. Havel, Y. Gogotsi, Monitoring Oxidation of Multiwalled Carbon Nanotubes by Raman Spectroscopy, *J. Raman Spectrosc.*, 38 (2007) 728-736.
- [32] M.S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, R. Saito, Perspectives on Carbon Nanotubes and Graphene Raman Spectroscopy, *Nano Lett.*, 10 (2010) 751-758.

- [33] S.A. Chernyak, A.S. Ivanov, K.I. Maslakov, A.V. Egorov, Z. Shen, S.S. Savilov, et al., Oxidation, defunctionalization and catalyst life cycle of carbon nanotubes: a Raman spectroscopy view, *Phys. Chem. Chem. Phys.*, 19 (2017) 2276-2285.
- [34] E.A. Arkhipova, A.S. Ivanov, N.E. Strokova, S.A. Chernyak, A.V. Shumyantsev, K.I. Maslakov, et al., Structural evolution of nitrogen-doped carbon nanotubes: From synthesis and oxidation to thermal defunctionalization, *Carbon*, 125 (2017) 20-31.
- [35] M.W. Smith, I. Dallmeyer, T.J. Johnson, C.S. Brauer, J.-S. McEwen, J.F. Espinal, et al., Structural analysis of char by Raman spectroscopy: Improving band assignments through computational calculations from first principles, *Carbon*, 100 (2016) 678-692.
- [36] K. Xie, F. Yang, P. Ebbinghaus, A. Erbe, M. Muhler, W. Xia, A reevaluation of the correlation between the synthesis parameters and structure and properties of nitrogen-doped carbon nanotubes, *J. Energy Chem.*, 24 (2015) 407-415.
- [37] G. Wu, C.M. Johnston, N.H. Mack, K. Artyushkova, M. Ferrandon, M. Nelson, et al., Synthesis–structure–performance correlation for polyaniline–Me–C non-precious metal cathode catalysts for oxygen reduction in fuel cells, *J. Mater. Chem.*, 21 (2011) 11392-11405.
- [38] J. Csontos, Z. Pápa, A. Gárdián, M. Füle, J. Budai, Z. Toth, Spectroscopic ellipsometric and Raman spectroscopic investigations of pulsed laser treated glassy carbon surfaces, *Appl. Surf. Sci.*, 336 (2015) 343-348.
- [39] S.A. Chernyak, A.S. Ivanov, N.E. Strokova, K.I. Maslakov, S.V. Savilov, V.V. Lunin, Mechanism of Thermal Defunctionalization of Oxidized Carbon Nanotubes, *J. Phys. Chem. C*, 120 (2016) 17465-17474.
- [40] S.A. Chernyak, A.S. Ivanov, E.A. Arkhipova, A.V. Shumyantsev, N.E. Strokova, K.I. Maslakov, et al., Mechanism and kinetics of decomposition of N-containing functional groups in few-layer graphene nanoflakes, *Appl. Surf. Sci.*, 484 (2019) 228-236.

- [41] S.V. Klovov, E.S. Lokteva, E.V. Golubina, K.I. Maslakov, A.V. Levanov, S.A. Chernyak, et al., Effective Pd/C catalyst for chlorobenzene and hexachlorobenzene hydrodechlorination by direct pyrolysis of sawdust impregnated with palladium nitrate, *Catal. Commun.*, 77 (2016) 37-41.
- [42] S.A. Chernyak, E.V. Suslova, A.S. Ivanov, A.V. Egorov, K.I. Maslakov, S.V. Savilov, et al., Co Catalysts Supported on Oxidized CNTs: Evolution of Structure during Preparation, Reduction and Catalytic Test in Fischer-Tropsch Synthesis, *Appl. Catal. A*, 523 (2016) 221-229.
- [43] M. Nakamizo, K. Tamai, Raman spectra of the oxidized and polished surfaces of carbon, *Carbon*, 22 (1984) 197-198.
- [44] A. Cuesta, P. Dhamelincourt, J. Laureyns, A. Martínez-Alonso, J.M.D. Tascón, Raman microprobe studies on carbon materials, *Carbon*, 32 (1994) 1523-1532.
- [45] A.C. Ferrari, J. Robertson, Origin of the 1150-cm⁻¹ Raman mode in nanocrystalline diamond, *Physical Review B*, 63 (2001) 121405.
- [46] R.J. Nemanich, S.A. Solin, First- and second-order Raman scattering from finite-size crystals of graphite, *Physical Review B*, 20 (1979) 392-401.
- [47] A. Yoshida, Y. Kaburagi, Y. Hishiyama, Full width at half maximum intensity of the G band in the first order Raman spectrum of carbon material as a parameter for graphitization, *Carbon*, 44 (2006) 2333-2335.
- [48] A.C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, *Physical Review B*, 61 (2000) 14095-14107.
- [49] J.N. Rouzaud, A. Oberlin, C. Beny-Bassez, Carbon films: Structure and microtexture (optical and electron microscopy, Raman spectroscopy), *Thin Solid Films*, 105 (1983) 75-96.
- [50] S.K. Sze, N. Siddique, J.J. Sloan, R. Escribano, Raman spectroscopic characterization of carbonaceous aerosols, *Atmos. Environ.*, 35 (2001) 561-568.

- [51] S.V. Saviolov, S.A. Chernyak, M.S. Paslova, A.S. Ivanov, T.B. Egorova, K.I. Maslakov, et al., 3D Frameworks with Variable Magnetic and Electrical Features from Sintered Cobalt-Modified Carbon Nanotubes, *ACS Appl. Mater. Interfaces*, 10 (2018) 20983-20994.
- [52] J. Ribeiro-Soares, M.E. Oliveros, C. Garin, M.V. David, L.G.P. Martins, C.A. Almeida, et al., Structural analysis of polycrystalline graphene systems by Raman spectroscopy, *Carbon*, 95 (2015) 646-652.
- [53] J.-B. Wu, M.-L. Lin, X. Cong, H.-N. Liu, P.-H. Tan, Raman spectroscopy of graphene-based materials and its applications in related devices, *Chem. Soc. Rev.*, 47 (2018) 1822-1873.
- [54] K. Sato, R. Saito, Y. Oyama, J. Jiang, L.G. Cançado, M.A. Pimenta, et al., D-band Raman intensity of graphitic materials as a function of laser energy and crystallite size, *Chem. Phys. Lett.*, 427 (2006) 117-121.
- [55] A.C. Ferrari, Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects, *Solid State Commun.*, 143 (2007) 47-57.
- [56] L. Gustavo Cançado, M. Gomes da Silva, E.H. Martins Ferreira, F. Hof, K. Kampioti, K. Huang, et al., Disentangling contributions of point and line defects in the Raman spectra of graphene-related materials, *2D Materials*, 4 (2017) 025039.
- [57] L.G. Cançado, A. Jorio, M.A. Pimenta, Measuring the absolute Raman cross section of nanographites as a function of laser energy and crystallite size, *Physical Review B*, 76 (2007) 064304.
- [58] A. Jorio, L.G. Cancado, Perspectives on Raman spectroscopy of graphene-based systems: from the perfect two-dimensional surface to charcoal, *Phys. Chem. Chem. Phys.*, 14 (2012) 15246-15256.
- [59] S. Praver, K.W. Nugent, D.N. Jamieson, J.O. Orwa, L.A. Bursill, J.L. Peng, The Raman spectrum of nanocrystalline diamond, *Chem. Phys. Lett.*, 332 (2000) 93-97.
- [60] Z. Xing, Z. Ju, Y. Zhao, J. Wan, Y. Zhu, Y. Qiang, et al., One-pot hydrothermal synthesis of Nitrogen-doped graphene as high-performance anode materials for lithium ion batteries, *Scientific Reports*, 6 (2016) 26146.

- [61] Y.-H. Tian, J. Huang, X. Sheng, B.G. Sumpter, M. Yoon, M. Kertesz, Nitrogen Doping Enables Covalent-Like π - π Bonding between Graphenes, *Nano Lett.*, 15 (2015) 5482-5491.
- [62] Z. Chaohua, F. Lei, L. Nan, L. Minhao, W. Yayu, L. Zhongfan, Synthesis of Nitrogen-Doped Graphene Using Embedded Carbon and Nitrogen Sources, *Adv. Mater.*, 23 (2011) 1020-1024.
- [63] S.V. Savilov, E.A. Arkhipova, A.S. Ivanov, K.I. Maslakov, Z. Shen, S.M. Aldoshin, et al., Pyrolytic synthesis and characterization of N-doped carbon nanoflakes for electrochemical applications, *Mater. Res. Bull.*, 69 (2015) 7-12.

Supplementary Material for on-line publication only

[Click here to download Supplementary Material for on-line publication only: Supporting Information.docx](#)

N-doping and oxidation of carbon nanotubes and jellyfish-like graphene nanoflakes through the prism of Raman spectroscopy

Sergei A. Chernyak^{a}, Anton S. Ivanov^a, Dmitrii N. Stolbov^{a,b}, Tolganay B. Egorova^a,
Konstantin I. Maslakov^a, Zexiang Shen^c, Valery V. Lunin^a, Serguei V. Savilov^a*

^a Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1–3, Moscow,
119991, Russia

^b Ivanovo State University, Nanomaterials Research Institute, Ermak str., 37/7, 153025, Ivanovo,
Russia

^c Division of Physics and Applied Physics, School of Physical and Mathematical Sciences,
Nanyang Technological University, Singapore 637371, Singapore

* Corresponding author. E-mail: chernyak.msu@gmail.com

Present work demonstrates the differences between the structure and surface transformations of carbon nanotubes (CNTs) and graphene nanoflakes with small particle size (GNFs) under oxidation and N-doping using Raman spectra processing. Jellyfish-like GNFs are rather new material that differs from the commonly known graphene nanoflakes by rounded edges and small size of particles (less than 50 nm). This material is promising in electrochemistry due to its high specific capacitance. It was found that, despite the graphene nature of both CNTs and GNFs, their Raman spectra change differently under oxidation and N-doping because of the different growth mechanisms of CNTs and GNFs, strong curvature of carbon layers in CNTs, and a large number of edge carbon atoms in GNFs.

Keywords: carbon nanotubes; graphene nanoflakes; Raman spectroscopy; oxidation; N-doping

1. Introduction

Structured carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene are promising or have proven to be successful for use in composites, microelectronics, energy storage devices, sensors, catalysts and biomedicine [1, 2]. Some of these applications require structural or surface modification of carbon nanomaterials. For example, preparation of polymer composites with CNTs or their surface decoration with metal nanoparticles includes functionalization of the CNT surface usually achieved by oxidative treatment [3, 4]. The electronic properties of CNTs or graphene materials can be tuned by heterosubstitution of carbon atoms [5, 6]: nitrogen, boron, sulfur, and silicon atoms can be introduced in graphene sheets to change both the surface and bulk properties of the material [7, 8]. Nitrogen is the most popular dopant for CNTs and graphene because the size of N atoms is close to that of C ones whereas N-containing precursors are cheap and safe to use, and the synthesized materials are stable in air. Doped carbon nanomaterials show the promising properties in energy storage, electro- and heterogeneous catalysis, sensing devices, and fuel cells [9, 10].

Graphite exfoliation produces graphene nanoflakes or nanosheets with the domain size from hundreds of nanometers to microns [11-13]. These materials are usually studied for electrochemical [14], opto-electronic [15], and catalytic [16] applications. At the same time, N-doped small-size GNFs less than 50 nm in diameter obtained directly by hydrocarbon pyrolysis [17, 18] showed the promising properties in the electrode material of supercapacitors [19]. The main benefit of this synthesis technique is that GNFs with rather narrow size distribution and low stacking number of graphene layers can be synthesized in one stage and their purification does not require using sulfuric acid and potassium permanganate. The edges of these GNFs are rounded, so their shape resembles jellyfish [17].

Raman spectroscopy is a widely used technique to study graphene-based materials [20, 21]. It allows revealing their structure, the degree of graphitization, the presence of defects and amorphous impurities, etc [22-24]. In 1970 Tuinstra and Koenig published Raman spectroscopy study of graphite and

1 postulated that a single crystal produces only one Raman band at $\sim 1575\text{ cm}^{-1}$ attributed to E_{2g} stretching
2 vibrations of graphite lattice of the infinite crystal [25]. Another band appeared at 1355 cm^{-1} in the
3 Raman spectrum of polycrystalline graphite is associated with the A_{1g} mode of the lattice [26]. This band
4 was established to originate not from the disordered carbon but from small crystallites or boundaries of
5 large crystals. Later it was shown that the D band originates from the double resonant process [27, 28]
6 and appears in Raman spectra of structured nanocarbons when the symmetry of the graphite unit cell is
7 broken by an edge atom or heteroatom [29, 30]. These two bands were named as G and D band,
8 respectively. The I_D/I_G intensity ratio is usually used as a parameter of the defectiveness of the carbon
9 material [31]. The 2D (G') band observed in Raman spectra of graphitic materials at $\sim 2700\text{ cm}^{-1}$ results
10 from a second-order two-phonon process, that is, this band is the D band overtone [32]. The 2G band is
11 always observed in the spectra because it originates from a process where the momentum conservation is
12 satisfied by two phonons with the opposite wave vectors; therefore no defects are required for the
13 phonons activation [22]. Parameters of the Raman spectrum of a graphitic material correlate with its
14 defectiveness that depends both on the synthesis conditions and further treatment (oxidation,
15 functionalization, annealing, etc.). But usually only the I_D/I_G and I_G/I_G ratios are considered as indicators
16 of the defectiveness of carbon material though much more information could be extracted from the
17 spectra [23, 33-38]. However, because a plenty of carbon materials show similar Raman spectra, these
18 spectra cannot be unambiguously interpreted and other techniques, such as TEM, XPS, XRD, etc. are
19 required to draw clear conclusions.

20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47 This study is devoted to the comparative Raman spectroscopy analysis of two types of materials
48 constructed from graphene planes: multi-walled CNTs, small-size few-layer graphene nanoflakes (GNFs),
49 and their N-doped and oxidized derivatives. Though nanoparticles of both materials consist of several
50 graphene layers, CNTs are 1D material, while GNFs can be attributed to “quazi-2D” one. The Raman
51 spectra of CNTs and GNFs show many differences. Moreover, diverse location and orientation of
52
53
54
55
56
57
58
59
60
61
62
63
64
65

graphene layers lead to a significant contrast in the transformations of Raman spectra under N-doping and oxidative treatment.

2. Experimental

2.1. Preparation of materials

Multi-walled CNTs and N-CNTs were synthesized by the pyrolysis of hexane or acetonitrile over the Co-Mo/MgO catalyst in a quartz tubular reactor at 750°C. The synthesis details may be found in [39] for CNTs and in [34] for N-CNTs. In brief, nitrogen, bubbled through hexane or acetonitrile, was passed for 5 h over the catalyst prepared from cobalt and magnesium nitrates and ammonium molybdate. GNFs and N-GNFs were produced by the pyrolysis of the hexane or acetonitrile precursors for 30 min over the MgO template in a quartz tubular reactor at 800°C under the flow of nitrogen bubbled through the precursor. The MgO template was obtained from magnesium oxalate. Further details of the GNFs and N-GNFs syntheses may be found in [17] and [40], respectively. All the synthesized materials were purified from the catalyst/template and amorphous impurities by refluxing in 18% HCl water solution for 4 h followed by washing with distilled water until neutral pH, drying at 130°C and annealing in air at 350°C for 1 h. The purified samples were named as “CNT”, “GNF”, “N-CNT”, and “N-GNF”. Coal was produced by pyrolysis of birch sawdust in N₂ flow at 430 °C in an oven heated tubular quartz reactor described elsewhere [41].

The CNT and GNF materials were oxidized by refluxing in concentrated HNO₃ water solution, washed with distilled water until neutral pH and dried at 110°C. Pristine and N-doped carbon materials show different behavior under oxidation because of the higher defectiveness of N-doped graphene layers. For example, it was previously demonstrated that the maximum oxygen content in undoped CNTs was achieved after 3–6 h of nitric acid treatment [42] while that in N-doped CNTs was observed at oxidation time of 0.5–1 h, with the nitrogen content being strongly decreased during further oxidation [34]. That is

why the different oxidation times were chosen for the undoped and N-doped materials: 3 and 1 h, respectively. The oxidized materials were named as “CNTox”, “GNFox”, “N-CNTox”, and “N-GNFox”.

2.2. Characterization

Raman spectra of the samples were registered using a LabRam HR800 UV (Horiba Jobin Yvon, Japan) microscope-spectrometer (5 mW argon laser excitation with 514.5 nm wavelength and 50× Olympus lens). At least four spectra were acquired for each sample (Fig.S1–S8). OriginLab software was used for curve fitting. The number of components was chosen according to the fitting model (see Section 3.2). During fitting the positions of the D3 and D4 bands were restricted in the ranges of 1500–1515 cm^{-1} and <1300 cm^{-1} , respectively, while the FWHMs for all bands were not fixed.

The specific surface area of the materials was measured by low temperature nitrogen adsorption using a Quantachrome AUTOSORB-1C/MS/TPR gas sorption analyzer. Prior to analysis, samples were degassed at 250°C for 3 h under vacuum. X-ray diffraction (XRD) patterns were recorded in the 2 θ range of 10° to 70° using a Stoe Stadi P instrument equipped with a Ni-filtered CuK α X-ray tube. The interlayer distances were calculated using Bragg’s law. The position and FWHM of the graphitic (002) reflection were obtained by curve fitting of the XRD diffraction pattern using the Pseudo-Voight profile. The morphology and structure of the samples were studied using a JEOL 2100F/Cs transmission electron microscope (TEM). Electron diffraction patterns were registered using selected area electron diffraction (SAED). The oxygen and nitrogen contents in the samples were determined using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS) with a monochromatic Al K α source ($h\nu = 1486.7 \text{ eV}$, 150 W).

The BET specific surface area and the N and O contents in the samples are shown in Table 1.

Table 1. Specific surface area (S_{BET}), XPS oxygen and nitrogen contents and N/C and O/C atomic ratios in the studied samples.

Sample	S_{BET} (m^2/g)	Oxygen (at.%)	Nitrogen (at.%)	O/C	N/C
CNT [42]	192	0.3	0	0.003	0
N-CNT	270	1.5	1.6	0.015	0.017
CNTox [42]	233	8.0	0.8	0.088	0.009
N-CNTox	200	7.1	1.1	0.077	0.012
GNF	1495	0.7	0	0.007	0
N-GNF	1036	3.3	9.6	0.038	0.110
GNFox	54	17.0	0.9	0.207	0.011
N-GNFox	120	10.0	8.5	0.123	0.104

3. Results and discussion

3.1. General characterization of pristine CNTs and GNFs

Both CNTs and GNFs consist of several graphene sheets. In the case of CNTs these sheets are rolled up and very long in axial direction, whereas in GNFs they are flat, smaller (less than 50 nm) and bent at the edges. TEM images show more perfect layered structure and uniform interlayer spacing in the case of pristine CNTs compared to GNFs (Fig.1). The graphitic structure persists even at bends of CNTs. At the same time, the variation of interlayer distance is observed within GNFs as a result of the distortion of layers.

Fig.1. TEM images of pristine CNTs (a,b) and GNFs (c,d).

XRD data confirm the difference in the graphitization degree between pristine CNTs and GNFs (Fig.2). The graphite (002) peak is clearly seen in the XRD pattern of CNTs at 25.7° in contrast to the broad peak at $\sim 23.2^\circ$ in the semi-amorphous pattern of GNFs. XRD data correlate with SAED patterns in which the graphite (002) reflections are observed in the case of CNTs (Fig.1a) whereas only amorphous halo is seen for GNFs (Fig.1c). The small peaks in the XRD patterns of GNFs samples at $\sim 21.9^\circ$ and 31.4° can be attributed to the residual SiO_2 (PDF card #71-821) from the quartz reactor used for synthesis. The presence of the halo and the asymmetric tail at the left side of the (002) peak in the XRD pattern of pristine GNFs correspond to the scattering of the interlayer distance towards higher values which is consistent with the SAED signal blurring towards the center of the pattern (Fig.1c). Therefore, on the base of TEM and XRD results it can be concluded that the CNT structure is more perfect compared to GNF one.

Fig.2. XRD profiles of graphitic (002) peak and calculated interlayer distances in the studied samples.

The structural differences between GNFs and graphite result from the small particle size and great amount of edge carbon atoms in GNFs that lead to a disorder in the arrangement of graphene layers, that is, to the partially turbostratic structure of particles. The difference in the structure of CNTs and GNFs determines the difference between their Raman spectra. Indeed, the strong broadening of the D-band at $\sim 1350 \text{ cm}^{-1}$ in the Raman spectrum of GNFs makes it similar to that of soot and coal, while the spectrum of CNTs is close to that of polycrystalline graphite (Fig.3).

Fig.3. Raman spectra of GNFs, CNTs, and their oxidized and N-doped derivatives. Coal spectrum is also shown for comparison.

3.2. Curve fitting of Raman spectra

Accurate characterization of the studied materials by Raman spectroscopy requires careful choosing of both the set of analyzed bands and the fitting model. The Raman spectra of CNTs and GNFs differ both in the range of 800–2000 and 2000–3500 cm^{-1} (Fig.3). In this work we will predominantly consider the former region because the latter one contains overtones of the G and D bands, which complicates the analysis. The 800–2000 cm^{-1} region of the CNT spectrum can be fitted by five components [30, 33]. Besides the main D1 and G peaks that correspond to edge carbon atoms and E_{2g} stretching vibrations of graphite lattice, respectively, three additional defect related peaks (D2, D3 and D4) can be also identified. These peaks are usually assigned to amorphous fraction, fragments of surface

graphene layers of CNTs (D3 and D4), stacking defects (D3), and small-size graphene clusters (D2) [30, 33-35]. Fitting parameters, such as intensities, areas and widths of the peaks or their ratios, allow tracing the structure differences between the studied materials. The Raman spectrum parameters considered in this work and their explanation are presented in Table 2. Along with the intensity ratios of the Raman peaks (bands) that are widely used for characterizing carbon nanomaterials, curve fitting of Raman spectra also yields the areas of the peaks. In contrast to the intensity ratios, the area ratios can provide more reliable information because the possible broadening of the peaks is taken into account. In this work we traced both the intensity and area ratios of the Raman bands and found that all trends were quite similar but more pronounced changes were observed for the area ratios. In case of GNFs there was no opportunity to fit the second order region (G' band), therefore, only the $I_{G'}/I_G$ intensity ratio was available.

Table 2. Raman spectral parameters considered in the present work and their interpretation on the base of works [25, 30, 31, 33-35, 43-51]. S, I, and W are, respectively, the area, intensity, and FWHM of the Raman band.

Parameter	Relation to the graphitic material structure and defects
S_{D1}/S_G	Carbon atoms with broken symmetry of the graphite cell (near edges, defects or heteroatoms)
S_{D3}/S_G	Polyene-/polyphenylene-type fragments (amorphous carbon) or stacking defects
S_{D4}/S_G	Polyene-/polyphenylene-type fragments (amorphous carbon)
$I_{G'}/I_G$	Interlayer defects
$W(D1) \text{ (cm}^{-1}\text{)}$	Structuring degree of the amorphous fraction
$W(G) \text{ (cm}^{-1}\text{)}$	Structuring degree of the graphitic fraction
$S(G) \text{ (%)}$	The fraction of the intact non-defective graphitic clusters (G band area relative to the total area of the 800–2000 cm^{-1} region)

According to the literature the most suitable function for fitting the 800–2000 cm^{-1} region in the Raman spectrum of CNTs is Lorentzian for the D1, D2, D4, G bands and mixed Gaussian–Lorentzian for the D3 band [30, 33, 34] (Fig.4).

Fig.4. Curve fittings of the 800–2000 cm^{-1} region in the Raman spectra of CNTs and GNFs. Two different fitting models were used for the GNFs spectrum. L, G and PV denote Lorentzian, Gaussian, and Pseudo-Voigt profiles, correspondingly.

The D2 band cannot be reliably extracted from the Raman spectrum of GNFs (Fig.4), which was previously pointed in [52]. This band corresponds to the central ring breathing mode with surrounding asymmetric stretch behavior in small-sized graphene fragments according to Smith et al. [35] and originates from intravalley one- and two-phonon Raman processes, respectively, involving one longitudinal optical phonon near the Γ point and one defect [53]. In the spectrum of GNFs the G band shifts to higher wavenumbers overlapping with the D2 band. Such overlapping under disordering of graphitic materials was also observed in [54-56] and the 2D2 band was used as an evidence of the D2 band presence. In the present study second-order region contains a broad peak between ~ 2300 and ~ 3300

cm⁻¹ that is difficult to fit due to the increased FWHMs of all components. The formation of the single G+D2 band in graphene oxide (GO) was also discussed in [53] as a result of the phonon quantum confinement effect induced by the small domain size in GO. Different fitting models may be applied to the Raman spectrum of GNFs, and we chose two sets of fitting functions depending on the way we consider this material (Fig.4).

- **Model I.** The D4, D1, and G bands are fitted with Lorentzian profiles, while the D3 band – with a Gaussian one, the same way as it was done for CNTs. In this model GNFs are considered as dispersed graphitic particles containing amorphous impurities (“top-down” approach). The difference between the application of this model to CNTs and GNFs is the presence of separate component for the D2 band in the former case.
- **Model II.** GNFs are treated as stacks of small diameter graphene clusters. If we accept the range of particle diameter of 10–50 nm and the largest diagonal of the benzene ring of 0.28 nm, the GNF diameter will correspond to a sequence of 36–179 benzene rings. In this case, we can use the curve fitting approach proposed for estimating the size of graphene fragments in coals [35]. In this approach the Gaussian profile was suggested for the D1, D3, and D4 bands while the mixed Lorentzian – Gaussian profile can be applied for the G band: smaller size of the graphene cluster leads to more Gaussian profile of the G band. In the present work we decided to use Pseudo-Voigt function for the fitting of the G band (Fig.4). The μ index in this function varies from 0 for the Gaussian profile to 1 for the Lorentzian one. Such an approach can be referred as “bottom-up” since GNF particles are considering not as a reduced graphite/graphene but as an “overgrown” coronene/ovalene/etc.

For a certain spectrum these different fitting models yield different sets of parameters that cannot be directly compared. Each model has its own advantages and disadvantages depending on the material nature and the objectives of the study. For example, in the case of pristine GNFs and their comparison

with other graphene-like materials (CNTs, graphene, and graphite) model I is more suitable because it makes possible to compare the intensity ratios of the D and G bands, their widths and positions in Raman spectra of different materials. At the same time, model II is more convenient for the comparison of pristine and doped GNFs (see chapter 3.4).

3.3. Results of curve fitting for undoped non-oxidized materials

The Raman spectra of all studied materials are presented in Fig.3. Fig.5 demonstrates the results of curve fitting of the CNT, GNF, CNTox, GNFox, N-CNT, and N-CNTox spectra using model I. The equation for the average in-plane crystallite size (L_a) of a nanostructured graphitic material proposed by Ribeiro-Soares et al. [52] can be applied to the GNF Raman spectrum fitted using model I (Lorentzian profile of the G band): $L_a = (l_c/2) * \ln[C/(W_G - W_G^\infty)]$, where l_c is the photon coherence length (~32 nm), C is the constant (95 cm^{-1}), W_G^∞ represents $W(G)$ for undoped pristine graphene (15 cm^{-1}). Another equation was proposed by Cançado et al. [57, 58]: $L_a \text{ (nm)} = 560/[W_G - 11]$. Both equations yield L_a for the pristine GNF sample in the range of 7–9 nm that is smaller than the particle size, which reflects the presence of defects inside graphene layers.

Fitting model I: D1, D2, D4, G - Lorentz; D3 - Gaussian

Fig.5. Results of curve fitting of the Raman spectra of CNTs and GNFs using model I (See section 3.2).

The results of curve fitting of the Raman spectra of pristine CNTs and GNFs indicate that CNTs are more structured material with higher degree of graphitization. Graphene layers in GNFs contain distortions of bond angles and lengths, which results in higher W(G), broader two-phonon bands, and lower S(G) for GNFs compared to CNTs despite the fact that graphene layers in CNTs are folded. Wider G band and higher S_{D3}/S_G, and S_{D4}/S_G ratios testify the significant amorphization of GNFs and layer bending in their structure. Lower I_G/I_G ratio in this case correlates with the deviation of the XRD interplanar distance from that of the ideal graphite structure. The significantly higher S_{D1}/S_G ratio for GNFs reflects the great number of edge carbon atoms. Similar Raman spectra were obtained in work [52] for the polycrystalline graphite samples with different in-plane crystallite size (L_a) of 3.8–17 nm.

Finally, it is worth noting that the G band in GNFs is strongly shifted towards higher wave numbers up to 1600 cm^{-1} . Its position is close to that of the D2 band corresponded to vibrations of central ring in polyaromatic fragments or small graphene clusters [35, 43] or graphene lattice vibrations involving only surface layers, and hence can represent the high surface-to-volume ratio [50, 59]. Thus, it can be proposed that some “averaged” G–D2 band is observed in the Raman spectrum of GNFs because of the small diameter and thickness of particles, which is consistent with work [55].

3.4. *N-doping of CNTs and GNFs*

N-doping of CNTs is known to result in the appearance of bamboo-like structure (Fig.6). The use of acetonitrile as a precursor in the CVD synthesis allowed introducing 2–3 at.% of nitrogen into CNTs (Table 1) and turn their cylindrical structure into bamboo-like one [34].

Fig.6. TEM images and SAED patterns of N-CNTs (a,b) and N-GNFs (c,d).

Though the Raman spectra of CNTs and N-CNTs are similar (Fig.3), curve fitting reveals some differences between these materials. The G band in N-CNTs is shifted to higher wave numbers (Fig.5d). Lower relative area of this band, higher S_{D3}/S_G , S_{D4}/S_G , and S_{D1}/S_G ratios and broader D1 band (Fig.5a,b,c) testify the slightly lower graphitization degree of N-CNTs compared to pristine CNTs.

These results along with the similar values (within the experimental error) of both the I_G/I_G ratio (Fig.5c) and the interplanar distance (Fig.2) for CNTs and N-CNTs demonstrate that doping with nitrogen adds extra curvatures and defect sites into the structure of CNTs but do not significantly affect their layered structure.

The Raman spectrum of N-doped GNFs, as well as the spectrum of pristine GNFs, is close to that of amorphous carbon and coal (Fig.3). The SAED patterns of GNFs and N-GNFs are also close (Fig.1c and 5c, respectively). Similar Raman spectra were obtained for large-size (300–500 nm) N-GNFs hydrothermally synthesized over MgO template [60]. Careful processing of the N-GNF Raman spectrum revealed that the “top-down” fitting approach (model I) was not applicable in this case (See the comparison between the model I and II curve fittings for the N-GNF sample in Fig.S9a,b). Therefore, this spectrum was analyzed using only the “bottom up” approach (model II) and the spectrum of pristine GNFs was processed the same way to correctly compare these materials. Such inapplicability of model I can be explained by the structure of N-GNFs in which polyaromatic graphene domains are separated by N atoms (see the discussion of Fig.8). It should be noted that model II cannot be used for N-CNTs because of the uncertainty of the D2 band position in the case of the Pseudo-Voigt profile of the G-band (See the comparison between model I and II fittings with the D2 band component for N-GNT sample in Fig.S9c,d). Fig. 7 shows the results of curve fitting of the Raman spectra of GNFs and N-GNFs. The broadening of the D and G bands after N-doping of GNFs is clearly seen while the relative area of the G band does not change within the experimental error. N-doping leads to the distortion of the angles and lengths of C–C bonds in the aromatic ring, but at the same time it does not affect the overall graphitic structure and morphology of the particles. The latter statement is also proved by the XRD data (Fig.2) and the I_G/I_G ratio (Fig.7b): interlayer distance in N-GNFs is even smaller and slightly closer to that in graphite than to that in pristine GNFs; the I_G/I_G ratio for N-GNFs is higher than that for the undoped material. On the other hand, the concentration of defects in N-GNFs is higher compared to pristine GNFs. It was theoretically calculated that the N-doped graphenes with various doping levels can form an unusual

two-dimensional π - π bonding in a bilayer, bringing the neighboring N-doped graphenes to significantly reduced interlayer separations [61]. Moreover, this effect becomes more pronounced with the increase in the N content up to ~12–13 at.% that is close to that in the N-GNF sample. The S_{D4}/S_G ratio within the experimental error doesn't change after N-doping. The S_{D3}/S_G and S_{D1}/S_G ratios increase because of the amorphization of the material and breaking of graphitic lattice symmetry by heteroatoms (Fig.7b). It is worth noting that the average particle sizes of GNFs and N-GNFs are rather similar: 21.9 ± 0.9 and 23.6 ± 0.9 nm, respectively (according to TEM, see Fig.S10), therefore, the difference in the S_{D1}/S_G ratio originates from nitrogen doping rather from the size effect.

Fig.7. Results of curve fitting of the Raman spectra of GNFs using model II (See section 3.2).

The L_a cannot be calculated for N-GNFs because it is impossible to fit the G band with the Lorentzian profile. At the same time higher W(G) for this sample compared to pristine GNFs reflects the decrease of L_a as a result of the incorporation of N atoms into graphene layers. Interestingly, the growth of the S_{D1}/S_G ratio is not so sharp in contrast to that observed under N-doping of graphene [62]. This can be explained by the high initial concentration of defects in GNFs compared to graphene, which makes it difficult to reveal the N-doping effect. Summarizing the above presented results it can be concluded that

N-doping of GNFs at the pyrolysis stage introduces planar defects and slightly changes the layer structure.

Let's consider a graphene fragment containing 110 carbon atoms (42 rings) (Fig.8a). Typically, the nitrogen content in N-doped GNFs varies in the range of 9–12 at.% according to XPS and elemental analysis [63]. In the present study N-GNF sample contains 9.6 at.% of N (Table 1), which corresponds to the substitution in the considered fragment of about 10 carbon atoms with nitrogen ones. The resulted N-doped GNF fragment may be divided into undoped domains containing N atoms only on their boundaries (Fig.8b). It should be also taken into account that pyridine and pyrrole nitrogen species are also present in N-GNFs [40], which introduces additional edges at the domain boundaries (Fig.8c).

Fig.8. Graphene fragment in GNF before (a) and after N-doping (b,c) that introduces into this fragment only graphitic/quaternary (b) or graphitic/quaternary, pyrrolic, and pyridinic (c) nitrogen species. The undoped graphene domains confined by nitrogen atoms are shown in N-doped GNF fragments.

As it was discussed in Section 3.2, in the case of coals the possibility of G band fitting with a Lorentzian profile for large graphitic fragments and with a Gaussian one for nanodispersed graphene clusters was considered in [35]. As N-doping divides a graphene layer into smaller unsubstituted domains (polyaromatic fragments), the Pseudo-Voigt function may be applied to estimate the nitrogen content in

N-GNFs. The μ coefficient in this function represents the Gaussian–Lorentzian ratio and varies from 0 for the Gaussian to 1 for the Lorentzian profiles. We can assume that the decrease in the domain size changes the G band profile to more Gaussian, that is, μ is expected to decrease with N-doping of GNFs. Therefore, it may be possible to trace N-doping using the μ coefficient of the Pseudo-Voigt profile applied for fitting of the G band. Indeed, μ decreases after N-doping of GNFs (Fig. 9), which qualitatively proves the discussion above. At the same time, oxidation leads to the increase of μ , which correlates with the XRD and SAED data (Fig.3 and Fig.2c, Fig.6c, Fig.11a,d). Thus, the decrease of μ can be considered as a qualitative indicator of N-doping, that is, of amorphization of the material.

Fig.9. μ coefficient of Pseudo-Voigt profile of the G band in the Raman spectra of pristine, N-doped GNFs, and their oxidized derivatives. μ is equal to 1 for the Lorentzian and 0 for the Gaussian profiles.

3.5. Oxidation of CNTs and GNFs

CNT oxidation by nitric acid water solution was thoroughly studied in our previous work [33]. TEM images demonstrate cutting of nanotubes and destruction of the surface layers under oxidation (Fig.10 a-c).

Fig.10. TEM images of CNTox (a-c) and N-CNTox (d-f).

Several simultaneous processes occur during CNT oxidation, including complete oxidation of the amorphous fraction and thin or short CNTs, exfoliation of surface layers, cutting of long nanotubes, and opening of channels [33]. As a result, the increase in the number of edge carbon atoms and the appearance of fragments of the destroyed upper layers, on the one hand, and the structuring of material, on the other hand, lead to the changes in the Raman spectra of CNTs under oxidation (Fig.5a). During oxidation the impact of the defects introduced by amorphous particles and CNT bends is replaced by that of fragments of the destroyed upper layers. As a result, the most structured CNTs remain in the sample. Therefore, the total number of defects increases, but the widths of the D1 and G bands in the Raman spectrum decrease. For example, the width of the G band for the oxidized CNTs is close to that for graphite (less than 50 cm^{-1}). The slight up-shift of the G band also indicates the formation of exfoliated

1 fragments (Fig.5d). In other words, oxidized CNTs contain well-ordered nanotubes covered with the great
2 number of exfoliated fragments.
3
4

5 N-doped CNTs are oxidized faster than pristine ones because of their higher defectiveness and
6 curvature [34]. After nitric acid treatment the S_{D1}/S_G and S_{D3}/S_G ratios grow while the S_{D4}/S_G one doesn't
7 change or even decreases (Fig.5b,c). The FWHMs of the G and D1 bands only slightly grow (in fact
8 insignificantly within the experimental error) because several simultaneous processes, such as gradual
9 oxidation of inner "bridges" (Fig.10e), destroying of surface layers (Fig.10f), cutting of nanotubes
10 (Fig.10d), and gasification of the most amorphous fragments, take place during N-CNT oxidation. These
11 processes seem to compensate each other. Actually, oxidation affects N-CNTs in a different way than the
12 pristine CNTs: the interlayer distance and the G band position in N-CNT grow while the $W(G)$ parameter
13 of their Raman spectrum remains unchanged (Fig.5a).
14
15
16
17
18
19
20
21
22
23
24
25
26
27

28 Oxidation of both undoped and N-doped GNFs leads to the similar changes in their structure. In
29 this case in contrast to CNTs and N-CNTs the slight reduction in the number of stacking defects and those
30 responsible for the fragments of the destroyed surface layers is observed (Fig.7b). We assume that the
31 edges of both pristine and N-doped GNFs are bent and highly-defective. The nanoflakes in their turn are
32 randomly oriented to each other forming a low-density material. Two important processes occur during
33 oxidation: removal of the most amorphous or the smallest GNFs and the formation of dense macro-
34 particles in which nanoflakes are packed because of the high degree of their functionalization and the
35 affinity of functional groups to each other. The second process can be better illustrated by the sharp
36 decrease in the S_{BET} after acid treatment (Table 1). The total number of edge carbon atoms is unchanged
37 because oxidation mainly proceeds at edges rather than in planes. The overall structuring of both GNFs
38 and N-GNFs after oxidation is also confirmed by their electron diffraction patterns (Fig.2, Fig.11a, and
39 Fig.11d). At the same time, SAED shows slightly stronger amorphization of oxidized N-GNFs compared
40 to GNFs (see the continuous halo in the center of the diffraction pattern in Fig.11d). Raman data also
41 demonstrate a noticeable difference between the N-GNFOx and GNFOx samples: the spectrum of the
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

former one shows higher S_{D1}/S_G ratio and broader D1 and G bands. The interlayer distance in N-GNFOx calculated from XRD was closer to that in graphite than the interlayer distance in GNFOx while the electron diffraction patterns show the appearance of (101) graphitic ring in both cases but with more amorphous halo for N-GNFs (Fig.11a,d).

Fig.11. TEM images and SAED patterns of GNFOx (a-c) and N-GNFOx (d-e) samples. Arrows indicate the sites where the noticeable changes are observed after oxidation.

Thus, it can be summarized that the oxidation of CNTs and N-CNTs occurs in a slightly different way, while GNFs and N-GNFs show similar changes under this treatment.

Conclusions

The changes in the structure of carbon nanotubes and small-size jellyfish-like graphene nanoflakes under N-doping and oxidation have been studied by Raman spectroscopy. Low size of graphene

nanoflakes, their turbostratic orientation, and great amount of edge carbon atoms in GNFs determine their amorphous-like Raman spectra with the strong broadening of the D1 and G bands. Two different models were applied for curve fitting of the 800–2000 cm^{-1} region in the Raman spectra of GNFs based materials. In these models GNFs are considered as a highly dispersed graphene/graphite or as an “overgrown” coronene/ovalene/etc. Both models imply four Raman bands: D1, D3, D4, and G. The G band in GNFs is noticeably shifted towards higher wavenumbers compared to CNTs because of the small size of graphene domains.

N-doping of CNTs and GNFs does not significantly affect their layered structure but introduces a lot of defects into the layer: it changes bond angles and lengths and forms holes and new edges within layers. This results in the increase in the relative intensities of all disordered components in the Raman spectra. The most significant difference in the N-doping of CNTs and GNFs is that the heterosubstitution changes the CNT structure at the growth stage and introduces additional curvatures into nanotubes, while in the case of GNFs nitrogen doping produces only planar defects. In addition, great amount of nitrogen increases the interaction between particles and graphene layers of GNFs, which reduces the interlayer distance and slightly decreases the I_G/I_G ratio because of the elimination of interlayer defects. The Pseudo-Voigt profile of the G band was found to be sensitive to N-doping: the Lorentzian profile of the G band in GNFs changes to the mixed Gaussian–Lorentzian one after doping, while the opposite trend was observed after oxidation.

Oxidation occurs differently for CNTs and N-CNTs, while it demonstrates similarity for GNFs and N-GNFs. Though the graphitic structure of CNTs becomes more perfect under the acid treatment because of removal of the most curved and defect nanotubes, the overall concentration of intact graphitic clusters decreases. At the same time, in the case of GNFs, the noticeable graphitization takes place because of the significant reduction in the number of stacking and interlayer defects and those responsible for the fragmentation of surface layers. The important factor here is the compaction and densification of the material and the disappearance of the turbostratic particle orientation. The oxidation of N-CNTs

differs from that of undoped CNTs: the interlayer distance grows while the $W(G)$ parameter of the Raman spectrum does not change because of the inherent bamboo-like structure of N-CNT walls. Thus, in general, the difference between the oxidation of CNTs and GNFs can be explained as follows. In CNTs the oxidation leads to the destruction of surface layers and cutting of nanotubes. This results in the growth of the number of edge carbon atoms and defect fragments and, hence, the S_{D1}/S_G , S_{D3}/S_G , and S_{D4}/S_G ratios increase. Oxidation of GNFs seems to only remove the most amorphous particles, while the average size of GNFs and the number of the edge carbon atoms remains unchanged. As a result, the S_{D1}/S_G , S_{D3}/S_G , and S_{D4}/S_G ratios for oxidized GNFs and CNTs are close to each other.

The results of this work should be useful for the study of 1D and 2D graphene-based materials, and not only by Raman spectroscopy. Fitting model I as it is used in this work or with the additional component attributed to the D2 band can be applied to any graphitic-based material while model II is more suitable for amorphous carbons and highly-dispersed graphenes/graphites.

Acknowledgments

The authors thank Dr. O.Y. Isaikina for Raman spectroscopy study and Dr. A.V. Egorov for his help in TEM investigations. This work was supported by the Russian Science Foundation under grant No. 18-13-00217. The authors acknowledge support from "Nanochemistry and Nanomaterials" MSU Equipment Center acting under Lomonosov Moscow State University Program of Development.

References

- [1] M.F.L. De Volder, S.H. Tawfick, R.H. Baughman, J. Hart, Carbon Nanotubes: Present and Future Commercial Applications, *Science*, 339 (2013) 535-539.
- [2] Y. Zhu, H. Ji, H.-M. Cheng, R.S. Ruoff, Mass production and industrial applications of graphene materials, *National Science Review*, 5 (2018) 90-101.
- [3] N.G. Sahoo, S. Rana, J.W. Cho, L. Li, S.H. Chan, Polymer Nanocomposites Based on Functionalized Carbon Nanotubes, *Prog. Polym. Sci.*, 35 (2010) 837-867.

- [4] H. Xiong, L.L. Jewell, N.J. Coville, Shaped Carbons As Supports for the Catalytic Conversion of Syngas to Clean Fuels, *ACS Catalysis*, 5 (2015) 2640-2658.
- [5] Q. Liu, J. Zhong, Z. Sun, H. Mi, Cross-linked carbon networks constructed from N-doped nanosheets with enhanced performance for supercapacitors, *Appl. Surf. Sci.*, 396 (2017) 1326-1334.
- [6] J. Palomino, D. Varshney, B.R. Weiner, G. Morell, Study of the Structural Changes Undergone by Hybrid Nanostructured Si-CNTs Employed as an Anode Material in a Rechargeable Lithium-Ion Battery, *J. Phys. Chem. C*, 119 (2015) 21125-21134.
- [7] M. Hu, Z. Yao, X. Wang, Graphene-Based Nanomaterials for Catalysis, *Ind. Eng. Chem. Res.*, 56 (2017) 3477-3502.
- [8] W. Qian, X. Cui, R. Hao, Y. Hou, Z. Zhang, Facile Preparation of Nitrogen-Doped Few-Layer Graphene via Supercritical Reaction, *ACS Appl. Mater. Interfaces*, 3 (2011) 2259-2264.
- [9] M. Inagaki, M. Toyoda, Y. Soneda, T. Morishita, Nitrogen-doped carbon materials, *Carbon*, 132 (2018) 104-140.
- [10] Y. Fengkai, X. Wei, M. Artjom, M. Justus, H. Dirk, S. Ilya, et al., NH₃ Post-Treatment Induces High Activity of Co-Based Electrocatalysts Supported on Carbon Nanotubes for the Oxygen Evolution Reaction, *ChemElectroChem*, 4 (2017) 2091-2098.
- [11] H. Han, Y. Zhang, N. Wang, M.K. Samani, Y. Ni, Z.Y. Mijbil, et al., Functionalization mediates heat transport in graphene nanoflakes, *Nat. Commun.*, 7 (2016) 11281.
- [12] M. Kumar, B.E.K. Swamy, M.H.M. Asif, C.C. Viswanath, Preparation of alanine and tyrosine functionalized graphene oxide nanoflakes and their modified carbon paste electrodes for the determination of dopamine, *Appl. Surf. Sci.*, 399 (2017) 411-419.
- [13] V. Castagnola, W. Zhao, L. Boselli, M.C. Lo Giudice, F. Meder, E. Polo, et al., Biological recognition of graphene nanoflakes, *Nat. Commun.*, 9 (2018) 1577.

- [14] X. Li, K. Zhou, J. Zhou, J. Shen, M. Ye, CuS nanoplatelets arrays grown on graphene nanosheets as advanced electrode materials for supercapacitor applications, *Journal of Materials Science & Technology*, 34 (2018) 2342-2349.
- [15] S. Sanyal, A.K. Manna, S.K. Pati, BN-decorated graphene nanoflakes with tunable opto-electronic and charge transport properties, *J. Mater. Chem. C*, 2 (2014) 2918-2928.
- [16] J.-L. Meunier, N.-Y. Mendoza-Gonzalez, R. Pristavita, D. Binny, D. Berk, Two-Dimensional Geometry Control of Graphene Nanoflakes Produced by Thermal Plasma for Catalyst Applications, *Plasma Chem. Plasma Process.*, 34 (2014) 505-521.
- [17] S.A. Chernyak, A.M. Podgornova, E.A. Arkhipova, R.O. Novotortsev, T.B. Egorova, A.S. Ivanov, et al., Jellyfish-like few-layer graphene nanoflakes: Synthesis, oxidation, and hydrothermal N-doping, *Appl. Surf. Sci.*, 439 (2018) 371-373.
- [18] S.A. Chernyak, D.N. Stolbov, A.S. Ivanov, S.V. Klovov, T.B. Egorova, K.I. Maslakov, et al., Effect of type and localization of nitrogen in graphene nanoflake support on structure and catalytic performance of Co-based Fischer-Tropsch catalysts, *Catal. Today*, (2019).
- [19] E.A. Arkhipova, A.S. Ivanov, S.V. Savilov, K.I. Maslakov, S.A. Chernyak, Y.A. Tambovtseva, et al., Effect of nitrogen doping of graphene nanoflakes on their efficiency in supercapacitor applications, *Functional Materials Letters*, 11 (2018) 1840005.
- [20] A. Merlen, J. Buijnsters, C. Pardanaud, A Guide to and Review of the Use of Multiwavelength Raman Spectroscopy for Characterizing Defective Aromatic Carbon Solids: from Graphene to Amorphous Carbons, *Coatings*, 7 (2017) 153.
- [21] Y. Jiang, J. Wang, L. Malfatti, D. Carboni, N. Senes, P. Innocenzi, Highly durable graphene-mediated surface enhanced Raman scattering (G-SERS) nanocomposites for molecular detection, *Appl. Surf. Sci.*, 450 (2018) 451-460.
- [22] A.C. Ferrari, D.M. Basko, Raman spectroscopy as a versatile tool for studying the properties of graphene, *Nat Nano*, 8 (2013) 235-246.

- [23] S.L.H. Rebelo, A. Guedes, M.E. Szeftczyk, A.M. Pereira, J.P. Araujo, C. Freire, Progress in the Raman spectra analysis of covalently functionalized multiwalled carbon nanotubes: unraveling disorder in graphitic materials, *Phys. Chem. Chem. Phys.*, 18 (2016) 12784-12796.
- [24] M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, L.G. Cancado, A. Jorio, R. Saito, Studying disorder in graphite-based systems by Raman spectroscopy, *Phys. Chem. Chem. Phys.*, 9 (2007) 1276-1290.
- [25] F. Tuinstra, J.L. Koenig, Raman Spectrum of Graphite, *The Journal of Chemical Physics*, 53 (1970) 1126-1130.
- [26] E. Kusiak-Nejman, R.J. Wróbel, J. Kapica-Kozar, A. Wanag, K. Szymańska, E. Mijowska, et al., Hybrid carbon-TiO₂ spheres: Investigation of structure, morphology and spectroscopic studies, *Appl. Surf. Sci.*, (2018).
- [27] C. Thomsen, S. Reich, Double Resonant Raman Scattering in Graphite, *Phys. Rev. Lett.*, 85 (2000) 5214-5217.
- [28] C. Thomsen, S. Reich, Raman Scattering in Carbon Nanotubes, in: M. Cardona, R. Merlin (Eds.) *Light Scattering in Solid IX*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2007, pp. 115-234.
- [29] Y. Wang, D.C. Alsmeyer, R.L. McCreery, Raman spectroscopy of carbon materials: structural basis of observed spectra, *Chem. Mater.*, 2 (1990) 557-563.
- [30] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Pöschl, Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information, *Carbon*, 43 (2005) 1731-1742.
- [31] S. Osswald, M. Havel, Y. Gogotsi, Monitoring Oxidation of Multiwalled Carbon Nanotubes by Raman Spectroscopy, *J. Raman Spectrosc.*, 38 (2007) 728-736.
- [32] M.S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, R. Saito, Perspectives on Carbon Nanotubes and Graphene Raman Spectroscopy, *Nano Lett.*, 10 (2010) 751-758.

- [33] S.A. Chernyak, A.S. Ivanov, K.I. Maslakov, A.V. Egorov, Z. Shen, S.S. Savilov, et al., Oxidation, defunctionalization and catalyst life cycle of carbon nanotubes: a Raman spectroscopy view, *Phys. Chem. Chem. Phys.*, 19 (2017) 2276-2285.
- [34] E.A. Arkhipova, A.S. Ivanov, N.E. Strokova, S.A. Chernyak, A.V. Shumyantsev, K.I. Maslakov, et al., Structural evolution of nitrogen-doped carbon nanotubes: From synthesis and oxidation to thermal defunctionalization, *Carbon*, 125 (2017) 20-31.
- [35] M.W. Smith, I. Dallmeyer, T.J. Johnson, C.S. Brauer, J.-S. McEwen, J.F. Espinal, et al., Structural analysis of char by Raman spectroscopy: Improving band assignments through computational calculations from first principles, *Carbon*, 100 (2016) 678-692.
- [36] K. Xie, F. Yang, P. Ebbinghaus, A. Erbe, M. Muhler, W. Xia, A reevaluation of the correlation between the synthesis parameters and structure and properties of nitrogen-doped carbon nanotubes, *J. Energy Chem.*, 24 (2015) 407-415.
- [37] G. Wu, C.M. Johnston, N.H. Mack, K. Artyushkova, M. Ferrandon, M. Nelson, et al., Synthesis–structure–performance correlation for polyaniline–Me–C non-precious metal cathode catalysts for oxygen reduction in fuel cells, *J. Mater. Chem.*, 21 (2011) 11392-11405.
- [38] J. Csontos, Z. Pápa, A. Gárdián, M. Füle, J. Budai, Z. Toth, Spectroscopic ellipsometric and Raman spectroscopic investigations of pulsed laser treated glassy carbon surfaces, *Appl. Surf. Sci.*, 336 (2015) 343-348.
- [39] S.A. Chernyak, A.S. Ivanov, N.E. Strokova, K.I. Maslakov, S.V. Savilov, V.V. Lunin, Mechanism of Thermal Defunctionalization of Oxidized Carbon Nanotubes, *J. Phys. Chem. C*, 120 (2016) 17465-17474.
- [40] S.A. Chernyak, A.S. Ivanov, E.A. Arkhipova, A.V. Shumyantsev, N.E. Strokova, K.I. Maslakov, et al., Mechanism and kinetics of decomposition of N-containing functional groups in few-layer graphene nanoflakes, *Appl. Surf. Sci.*, 484 (2019) 228-236.

- [41] S.V. Klovov, E.S. Lokteva, E.V. Golubina, K.I. Maslakov, A.V. Levanov, S.A. Chernyak, et al., Effective Pd/C catalyst for chlorobenzene and hexachlorobenzene hydrodechlorination by direct pyrolysis of sawdust impregnated with palladium nitrate, *Catal. Commun.*, 77 (2016) 37-41.
- [42] S.A. Chernyak, E.V. Suslova, A.S. Ivanov, A.V. Egorov, K.I. Maslakov, S.V. Savilov, et al., Co Catalysts Supported on Oxidized CNTs: Evolution of Structure during Preparation, Reduction and Catalytic Test in Fischer-Tropsch Synthesis, *Appl. Catal. A*, 523 (2016) 221-229.
- [43] M. Nakamizo, K. Tamai, Raman spectra of the oxidized and polished surfaces of carbon, *Carbon*, 22 (1984) 197-198.
- [44] A. Cuesta, P. Dhamelinourt, J. Laureyns, A. Martínez-Alonso, J.M.D. Tascón, Raman microprobe studies on carbon materials, *Carbon*, 32 (1994) 1523-1532.
- [45] A.C. Ferrari, J. Robertson, Origin of the 1150-cm⁻¹ Raman mode in nanocrystalline diamond, *Physical Review B*, 63 (2001) 121405.
- [46] R.J. Nemanich, S.A. Solin, First- and second-order Raman scattering from finite-size crystals of graphite, *Physical Review B*, 20 (1979) 392-401.
- [47] A. Yoshida, Y. Kaburagi, Y. Hishiyama, Full width at half maximum intensity of the G band in the first order Raman spectrum of carbon material as a parameter for graphitization, *Carbon*, 44 (2006) 2333-2335.
- [48] A.C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, *Physical Review B*, 61 (2000) 14095-14107.
- [49] J.N. Rouzaud, A. Oberlin, C. Beny-Bassez, Carbon films: Structure and microtexture (optical and electron microscopy, Raman spectroscopy), *Thin Solid Films*, 105 (1983) 75-96.
- [50] S.K. Sze, N. Siddique, J.J. Sloan, R. Escribano, Raman spectroscopic characterization of carbonaceous aerosols, *Atmos. Environ.*, 35 (2001) 561-568.

- [51] S.V. Saviolov, S.A. Chernyak, M.S. Paslova, A.S. Ivanov, T.B. Egorova, K.I. Maslakov, et al., 3D Frameworks with Variable Magnetic and Electrical Features from Sintered Cobalt-Modified Carbon Nanotubes, *ACS Appl. Mater. Interfaces*, 10 (2018) 20983-20994.
- [52] J. Ribeiro-Soares, M.E. Oliveros, C. Garin, M.V. David, L.G.P. Martins, C.A. Almeida, et al., Structural analysis of polycrystalline graphene systems by Raman spectroscopy, *Carbon*, 95 (2015) 646-652.
- [53] J.-B. Wu, M.-L. Lin, X. Cong, H.-N. Liu, P.-H. Tan, Raman spectroscopy of graphene-based materials and its applications in related devices, *Chem. Soc. Rev.*, 47 (2018) 1822-1873.
- [54] K. Sato, R. Saito, Y. Oyama, J. Jiang, L.G. Cançado, M.A. Pimenta, et al., D-band Raman intensity of graphitic materials as a function of laser energy and crystallite size, *Chem. Phys. Lett.*, 427 (2006) 117-121.
- [55] A.C. Ferrari, Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects, *Solid State Commun.*, 143 (2007) 47-57.
- [56] L. Gustavo Cançado, M. Gomes da Silva, E.H. Martins Ferreira, F. Hof, K. Kampioti, K. Huang, et al., Disentangling contributions of point and line defects in the Raman spectra of graphene-related materials, *2D Materials*, 4 (2017) 025039.
- [57] L.G. Cançado, A. Jorio, M.A. Pimenta, Measuring the absolute Raman cross section of nanographites as a function of laser energy and crystallite size, *Physical Review B*, 76 (2007) 064304.
- [58] A. Jorio, L.G. Cancado, Perspectives on Raman spectroscopy of graphene-based systems: from the perfect two-dimensional surface to charcoal, *Phys. Chem. Chem. Phys.*, 14 (2012) 15246-15256.
- [59] S. Praver, K.W. Nugent, D.N. Jamieson, J.O. Orwa, L.A. Bursill, J.L. Peng, The Raman spectrum of nanocrystalline diamond, *Chem. Phys. Lett.*, 332 (2000) 93-97.
- [60] Z. Xing, Z. Ju, Y. Zhao, J. Wan, Y. Zhu, Y. Qiang, et al., One-pot hydrothermal synthesis of Nitrogen-doped graphene as high-performance anode materials for lithium ion batteries, *Scientific Reports*, 6 (2016) 26146.

- [61] Y.-H. Tian, J. Huang, X. Sheng, B.G. Sumpter, M. Yoon, M. Kertesz, Nitrogen Doping Enables Covalent-Like π - π Bonding between Graphenes, *Nano Lett.*, 15 (2015) 5482-5491.
- [62] Z. Chaohua, F. Lei, L. Nan, L. Minhao, W. Yayu, L. Zhongfan, Synthesis of Nitrogen-Doped Graphene Using Embedded Carbon and Nitrogen Sources, *Adv. Mater.*, 23 (2011) 1020-1024.
- [63] S.V. Savilov, E.A. Arkhipova, A.S. Ivanov, K.I. Maslakov, Z. Shen, S.M. Aldoshin, et al., Pyrolytic synthesis and characterization of N-doped carbon nanoflakes for electrochemical applications, *Mater. Res. Bull.*, 69 (2015) 7-12.