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Comparison of Synchrotron and Laboratory X-ray Sources in Photoelectron Spectroscopy Experiments for the Study of Nitrogen-Doped Carbon Nanotubes

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Abstract: The chemical composition and stoichiometry of vertically aligned arrays of nitrogendoped multi-walled carbon nanotubes (N-CNTs) were studied by photoelectron spectroscopy using laboratory and synchrotron X-ray sources. We performed careful deconvolution of high-resolution core-level spectra to quantify pyridine/pyrrole-like defects in N-CNTs, which are a key factor in the efficiency of the piezoelectric response for this material. It is shown that the XPS method makes it possible to estimate the concentration and type of nitrogen incorporation (qualitatively and quantitatively) in the "N-CNT/Mo electrode" system using both synchrotron and laboratory sources. The obtained results allow us to study the effect of the nickel catalytic layer thickness on the concentration of pyridine/pyrrole-like nitrogen and piezoelectric response in the nanotubes.

Keywords: XPS; synchrotron radiation; surface chemistry; spectra deconvolution; carbon nanotube; nitrogen; molybdenum oxide

1. Introduction

Recently, the X-ray photoelectron spectroscopy (XPS) method has been extensively used in modern material science, becoming the most frequently employed not only in the fundamental research of surface sciences and nanomaterials, but also in applied multidisciplinary areas of chemistry [1], biology [2,3], medicine [4,5], etc. The considerable interest of researchers in the XPS method is due to the possibility of obtaining information not only about the composition of the surface of solids, but also about its chemical state, which allows to improve synthesis recipes and develop new materials with desired functional properties. The combination of laboratory XPS analysis and synchrotron techniques allows us to solve a variety of questions in material science. In particular, the use of angle resolved XPS and photoelectron spectroscopy based on synchrotron sources with tunable photon energy in tandem allows to determine the distribution of elements in the surface and near-surface layers of multi-component structures with high accuracy [6–8].

The method of XPS is based on the photoelectric effect, a phenomenon in which X-rays are absorbed by the substance and an electron (photoelectron) is emitted into the vacuum, for which its energy is analyzed. This effect is described by the extended Einstein equation for the photoelectric effect and has the following form $hv = KE + BEj + \varphi$, where *KE* is the kinetic energy of the photoelectron, *BEj* is the electron binding energy at the j-electron level in the atom, and φ is the work function. The desired value in the equation is the binding energy—*BEj*, while the kinetic energy of the photoelectron is



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). determined experimentally. The binding energy of a photoelectron is a characteristic value for each electronic shell of an element of the substance; therefore, the XPS method makes it possible to perform a qualitative analysis of a solid. As a rule, the simplest task of XPS is reduced to recording spectra and comparing characteristic photoemission lines with existing databases, for example, with the most common NIST [9]. According to a review conducted by G. Greczynski and L. Haltman which considers the number of scientific articles in the Scopus database related to the XPS method, the number of published works is significantly increasing every year [10]. Among the authors of the research papers, there is a tendency to compare the experimental data with the data presented in published articles. This approach is quite justified since with technological progress, the accuracy of modern laboratory instruments increases, which makes it possible to achieve a better spectral resolution, comparable to the unique synchrotron Megascience class facilities. However, the growing popularity and availability of XPS unfortunately inevitably leads to a decrease both in the quality of results and their interpretation, which can lead to dramatic consequences in terms of the reproducibility of scientific results [11,12]. For correct interpretation of XPS data, researchers have to thoroughly understand the process of the interaction of ionizing radiation with matter, as well as to possess knowledge in the field of quantum chemistry, but often insufficient time is devoted to studying the basics of XPS, which leads to inadequate experiment planning. In the case of multicomponent material analysis, where the photoelectronic signal of the primary structure of the spectrum (core and Auger electron lines) may overlap with the signal of the secondary structure (spinorbit and multiple splitting, satellites and plasmons, etc.), the complexity of interpreting XPS data is greatly increased, and even in some cases, not possible at all. Careful experiment planning can help to not face such scenarios, in particular, to avoid overlapping of the photoelectron lines of the core and Auger electrons. In some cases, it is sufficient to select the appropriate energy of the exciting X-ray source, at which the Auger electron transition is impossible or shifted from the core photoelectron lines [13–17].

In recent years, the number of publications on XPS studies of nitrogen-doped carbon nanotubes (N-CNTs) has been rapidly increasing due to high prospects for the use of N-CNTs for energy conversion and storage [18–22]. The electrical properties and catalytic activity of N-CNTs significantly depend on the concentration of doping nitrogen and its distribution according to the incorporation type in the N-CNT structure between pyrrole-, graphite-, and pyridine-like nitrogen [23-27]. The method of XPS makes it possible to characterize with high accuracy the type of chemical bonds of doping nitrogen with carbon and to establish the dependence of the N-CNT properties on the type of nitrogen incorporation. Thus, pyridine-like nitrogen has been shown to increase the surface wetting and catalytic activity of N-CNTs to develop efficient catalysts and supercapacitors [28–30]. The pyrrole-like nitrogen introduces significant distortions into the nanotube structure due to the formation of five-atom rings and leads to the formation of bamboo-like defects [31,32]. Bamboo-like defects, in turn, can lead to the formation of anomalous piezoelectric properties in N-CNTs to develop nanogenerators [33–35]. In this case, the material of the lower electrode, on which the N-CNTs are grown, significantly affects the concentration of doping nitrogen and its distribution according to the incorporation type [36]. The maximum concentration of doping nitrogen is observed in N-CNTs grown on a Mo electrode [36]. This fact is due to the lowest interaction between the nitrogen precursor and Mo during the nanotube growth and the preferential incorporation of nitrogen into the nanotube structure rather than the lower electrode. However, difficulties arise due to the overlapping of N1s and $Mo3p_{3/2}$ photoelectron core lines during XPS analysis of the N-CNTs on a Mo electrode.

In this paper, using the XPS technique, we analyze a multicomponent system based on nitrogen doped multi-walled carbon nanotubes grown on a Mo substrate. We demonstrate step by step the process of interpreting data using laboratory and synchrotron X-ray radiation sources by precise deconvolution of overlapping N1s and Mo3p_{3/2} photoelectron core lines. From the point of view of the rationality of using synchrotron accelerator complexes, we carried out a comparative analysis of the results obtained from the study of

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a laboratory spectrometer and a synchrotron source. The results presented in our paper allow us to plan the experiment in detail at the stage of choosing between laboratory and accelerator instruments for the XPS method.

2. Materials and Methods

Experimental samples of N-CNTs were grown by plasma-enhanced chemical vapor deposition (PECVD) in acetylene and ammonia flows. The process gas flow ratio of acetylene and ammonia was 70 and 210 cm³/min, respectively. The temperature of the samples' growth was 645 °C. The p-Si (100) was used as substrate on the surface of which a Mo lower electrode film of 100 nm thick and a Ni catalytic layer film were deposited by magnetron sputtering using an AUTO 500 (BOC Edwards, Crawley, UK). The thickness of the nickel catalytic layer was 5 nm and 15 nm for S1 and S2 samples, respectively. The power of used plasma is 40 W. The growth time was 15 min.

As is known, the process of the N-CNT growth by the PECVD method consists of four stages: sample heating, activation of catalytic centers, growth of N-CNTs, and sample cooling. At the stage of heating, a mixture of argon gas with a flow of 40 cm³/min and ammonia with a flow of $15 \text{ cm}^3/\text{min}$ is supplied to the PECVD chamber. The pressure in the chamber is maintained at a level of 4.5 Torr. At this stage, fragmentation of the initial film of the catalytic layer occurs with the formation of catalytic centers; the geometric dimensions, density, and chemical composition of which affect the parameters of the grown N-CNTs. At the activation stage, the formed catalytic centers are subjected to additional holding in the ammonia flow (210 cm³/min) at a given temperature. As a result, partial or complete reduction of the catalytic center metal occurs. During the growth stage, acetylene and ammonia are supplied to the reaction chamber. At this stage, an important task is to take into account the interaction of acetylene and ammonia flows with a Mo lower electrode, since the formation of molybdenum nitrides and carbides affects the concentration of free carbon and nitrogen atoms on the catalytic center surface. The ratio of carbon and nitrogen concentrations is responsible for the degree of concentration and type of forming defects (pyridine-, graphite-, and pyrrole-like) in the substitution of carbon by nitrogen [31,33].

The characterization of geometric parameters and structure of the experimental samples was carried out by scanning electron microscopy (SEM) using Nova NanoLab 600 (FEI, Eindhoven, The Netherlands) in secondary electrons mode and by transmission electron microscopy (TEM) using Tecnai Osiris (FEI, Eindhoven, The Netherlands). The X-ray photoelectron spectroscopy measurements were carried out in ultrahigh vacuum (UHV) 10-10 mbar conditions using commercial K-Alpha Themo Scientific spectrometer (Thermo-Scientific, Waltham, MA, USA) with monochromatic Al K α (1486.6 eV) X-ray source and using synchrotron X-ray radiation source (850 eV) at the RGBL Dipole beamline of BESSY II Light Source—Helmholtz-Zentrum Berlin (HZB, Berlin, Germany) [37]. The survey spectra recorded in the binding energy region of -10-750 eV and the pass energy (PE) was set at 200 eV for Al K α X-ray source and 70 eV for the synchrotron radiation source, respectively. High-resolution spectra were recorded in fixed analyzer transmission (FAT) mode with PE = 30 eV. Energy scale calibration was performed by position of maxima Au 4f7/2 high-resolution spectra collected from a standard gold sample with 99.99% purity. We determined the exact photon energy value and subsequently determined the position of the spectra relative to the Fermi level, taking into account that the binding energy of the Au $4f_{7/2}$ photoelectrons of bulk gold is 84 eV.

High-resolution spectra data were collected with energy step size of 0.1 eV and number of scans n = 10 for Al K α source and 0.025 eV, 3 scans for synchrotron radiation source, respectively. For quantification, Shirley and Tougaard background functions and relative sensitivity factors (RSF) from Scofield libraries were chosen [38]. During the component analysis, the best shape of the fitted curves was achieved with a Lorentz/Gauss function mixture at the ratio of 40/60.

The piezoelectric response of the N-CNTs was studied using the method of force spectroscopy of atomic force microscopy (AFM) at the Ntegra probe nanolaboratory (NT-

MDT, Moscow, Russia). The piezoelectric response is a current flow between the grounded AFM probe and the strained N-CNT having surface potential during its deformation. The force value applied to the AFM probe increased from 0 to 2 μ N. The AFM probe was a silicon probe with a conductive TiN coating and a curvature radius at 35 nm.

3. Results and Discussion

Figure 1a,b shows SEM images of the N-CNT S1 and S2 samples. As can be seen, the density of N-CNTs in the array for the S1 sample is lower than for the S2 sample, while the geometric parameters of nanotubes are closed (Table 1). The aspect ratio of the nanotube length L to the diameter D is about 17 and 20 for samples S1 and S2, respectively. The survey XPS (Figure 1c,d) spectra show the main elemental composition of the sample surface, which includes carbon, oxygen, molybdenum, and nitrogen. The characteristic difference in the survey spectra obtained from different sources is the presence of oxygen O_{KLL} Auger electron transitions in the 337 eV region when using the 850 eV synchrotron radiation source (SRS) (Figure 1d). According to the principles of XPS and Auger electron spectroscopy, a change in the energy of the excitation source leads to a shift in the photoemission lines on the kinetic energy scale. The kinetic energy values of Auger electrons are an unchanged characteristic of the electronic structure, and is a fingerprint for each atom [39]. In the XPS method, we calculate the binding energies of core electrons, which do not depend on the energy of the excitation photon. Therefore, the Auger electron lines are shifted by an amount equal to the difference in excitation photon energies between the synchrotron and laboratory radiation sources (LRS) when converting to a binding energy scale:

$$h\nu_{(SRS)} - h\nu_{(LRS)} = \Delta KE$$
; 850 eV - 1486.6 eV = -636.6 eV.

Thus, the O_{KLL} line with the SRS is shifted on the binding energy scale relative to the O_{KLL} (973.3 eV) with the laboratory Al K α (1486.6 eV) source by -636.6 eV and takes a value of 336.7 eV. Similarly, there is a signal from the carbon C_{KLL} Auger electron line at 583 eV on the survey spectrum of the S2 sample (Figure 2d). In addition, the difference is also seen in the presence of peaks at 103.5 and 154.4 eV, which correspond to the photoemission lines of silicon bound to oxygen SiO_2 (Si2p and Si2s, respectively) [9]. We assume that the presence of a photoelectronic signal from silicon in the case of the S2 sample is due to the imperfection of the Mo electrode in the form of a local rupture of the interface with the surface of the silicon substrate. This fact may be due to the larger thickness of the catalytic layer and the denser array of N-CNTs (Figure 1b). This statement is supported by the fact that the analyzed depth in the SRS case is smaller than in the LRS. We estimated the depth of the analyzed layers by calculating the inelastic mean free path of electrons using the S. Tanuma, C. J. Powell, D. R. Penn (TPP-IMFP) algorithm [40]. Figure 2 shows the curves of TPP-IMFP dependence on photon energy for the compounds pyrrole-like (N5), piridine-like (N6), graphite-like nitrogen (NG), MoO₂, MoO₃, MoN, SiO₂, Ni, and Ni(OH)₂. Table 2 presents the values for their calculation.

Table 1. Geometric parameters and surface composition of the N-CNT samples before component analysis.

Sample	D, nm	L, µm	C1s, %	O1s, %	N1s, %	Mo3d, %
S1	117 ± 33	1.96 ± 0.4	40.14	21.77	25.25	12.84
S1	92 ± 41	1.81 ± 0.12	37.93	16.33	36.64	9.1

 S1	92 ± 41	1.81 ± 0.12	37.93	16.33	36.64	

Table 2. Parameters used for TPP-IMFP calculation.

Parameters	MoO ₂	MoO ₃	MoN	SiO ₂	Ni	Ni(OH) ₂	N5 *	N6 *	NG *	CO ₂
Density, g/cm^3	6.48	4.69	9.06	2.65	8.90	5.20	0.97	0.98	1.02	1.76
Bandgap, eV	2.53	3.30	0.00	8.60	0.00	4.10	0.59	0.41	0.21	6.63
Valence electrons	18	24	9	16	2	16	19	23	63.00	18

* N5—pyrrole-like, N6—pyridine-like and NG—graphite-like nitrogen.



Figure 1. SEM images, survey, and high-resolution spectra of a N-CNT grown at Mo electrode: (**a**,**c**,**e**)—S1 sample and (**b**,**d**,**f**)—S2 sample, respectively.

We excluded the interaction of silicon with the N-CNTs by analyzing the spectra of photoelectron lines C1s (Figure 3a blue curve) and Si2p (Figure 1f). The shapes and positions of the curves indicate the absence of Si-C bonds, which for the silicon line correspond to Si2p3 ~100.3 eV and for the carbon line C1s ~283 eV [9]. Furthermore, the temperature for silicon carbide formation (over 1500 °C) is much higher than nanotube growth (645 °C). This fact also excludes the formation of silicon carbide. The comprehensive analysis of N-CNTs using XPS and TEM methods allowed us to establish that a nickel catalyst in the form of nanoparticles diffuses into the nanotubes during N-CNT growth. This fact is confirmed by the weak Ni2p signal obtained from the AlKa source. Moreover, we did not detect a nickel photoelectron signal in the synchrotron experiments due to the fact that the

depth of the analyzed layer in the SRS with the excitation source at 850 eV is slightly lower than in the LRS with Al K α (1486.6 eV). This also indicates the diffusion of nickel particles into N-CNTs. Analysis of the presented high-resolution nickel Ni2p3 spectrum (with LRS at Al K α 1486.6 eV) (Figure 1e) indicates that the nickel particle has the form of a metallic nanocluster covered with hydroxide with characteristic components of Ni + 2 (855.7 eV) and Ni + 0 (853 eV) [41]. The poor photoelectron signal of Ni2p3 does not allow for a component analysis to accurately determine the amount of nickel hydroxide.



Figure 2. Curves of TPP-IMFP dependence on photon energy for the compounds N5, N6, NG, MoO₂, MoO₃, MoN, SiO₂, Ni, and Ni(OH)₂.



Figure 3. High-resolution spectra of C1s (**a**), O1s (**b**), N1s (**c**), and Mo3d (**d**) for the S1 sample—red curves and the S2 sample—blue curves, respectively. For the S1 sample, the data were collected using standard Al K α X-ray radiation source, and for the S2 sample using synchrotron radiation source.

In our calculations, we take into account the contribution of the photoelectron signal from silicon to the surface composition of N-CNTs by excluding the integral signal of the oxygen fraction that accounts for it. However, the concentration dependencies in Table 1 do not take into account the fraction of the signal that corresponds to the overlapping photoelectron lines of N1s and $Mo3p_{3/2}$. The S1 sample calculation of the element atom concentrations is carried out by determining the curve areas of the corresponding components and their normalization as follows:

$$S_{norm} = \frac{S_{peak}}{F_x T_x C_x}, \qquad N_{element} = \frac{S_{norm}}{\sum_{x=1}^{n} S_{norm}}$$

where $N_{element}$ —x-element concentration; S_{norm} —normalized area under the peak of the x-element; F_x —sensitivity factor of the x-element, which depends on the orbital; T_x —transmission function (depends on the sensitivity factor); C_x —attenuation length, correction for the free path length of non-elastically scattered electrons. The values F_x , T_x , and C_x are defined from the Scofield libraries. Quantification of the element atom concentrations for the synchrotron measurements of the S2 sample is carried out using J.J. Yeh and I. Lindau photoionization cross-section data [42] as follows:

$$C_x = \frac{I_x}{\sigma_x \times \rho_f}$$

where I_x —integral intensity of the x spectral line, σ_x —photoionization cross-section of x element spectral line, and ρ_f —photon flux.

As can be seen, the difference between the surface composition of the samples is the ratio of oxygen, nitrogen, and molybdenum. On the one hand, this is due to the morphology structure of the samples, where in the case of the S1 sample, the N-CNT density is lower, which indicates a larger signal from the Mo electrode; on the other hand, this is due to a calculation error related to the overlap of the N1s and Mo3p_{3/2} photoelectron lines.

To determine the composition of the surface in detail, it is necessary to use high-resolution spectra, which allows us to calculate more accurately the areas under the peaks. Figure 3a–d shows the high-resolution spectra of C1s, O1s, N1s, and Mo3d for the S1 sample—red curves and the S2 sample—blue curves, respectively. As can be seen, the shape and position of the intensity maxima of the photoelectron lines differ from sample to sample, which indicates a different stoichiometric ratio. The main task here is to separate the photoelectronic signal related to the core electrons N1s and Mo3p_{3/2}.

For this purpose, we deconvoluted the high-resolution spectra of Mo3d and determined the component composition of molybdenum (Figure 4a,b). According to the results of deconvolution, it was established that for both samples, molybdenum has a different degree of oxidation from Mo¹⁺ to Mo⁶⁺, while its oxides and nitrides were found. According to the literature sources, the fitted components of the Mo3d photoemission line correspond to MoN, MoO_2 , MoO_x , and MoO_3 (the position of the binding energies shown in Table 3) [43–46]. Table 4 shows the components and the concentration ratios obtained from the results of deconvolution of the high-resolution spectra of Mo3d. It is known that when chemical bonds are formed, a change in the energy states of the outer orbitals also leads to a change in the inner ones. In this regard, the ratio of the components for the Mo3p_{3/2} photoelectron lines should be proportional to the ratio of the Mo3d_{5/2} components. Applying the obtained concentration ratios of the molybdenum components for the photoelectron overlapping core lines of N1s and Mo $3p_{3/2}$, we deconvoluted the spectra (Figure 4c,d). The result of deconvoluting the high-resolution spectra of the overlapping of photoemission lines for N1s and Mo3p_{3/2} indicates the presence of components corresponding to the compounds MoN, MoO_2 , MoO_x , and MoO_3 (Table 4), which agrees with the results obtained in Figure 4a,b.



Figure 4. High-resolution spectra of Mo3d and N1s region (**a**,**c**)—for the S1 sample and (**b**,**d**)—for the S2 sample, respectively.

Table 3. Binding energies of the $Mo3d_{5/2}$ and N1s components versus literature sources.
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Sample		Mo3d _{5/2} Binding Energy, eV				N1s Binding Energy, eV					
	MoN	MoO ₂	MoO _x	MoO ₃	N5 *	N6 *	NG *	NP *	N-Mo *		
S1	229.0	229.44	231.24	232.75	399.81	398.49	400.81	402.20	396.80		
S2	229.0	229.47	231.70	232.86	399.80	399.0	401.20	402.85	397.16		
Lit.	228.95 [43]	229.4 [44]	231.90 [45]	232.70 [46]	399.80 [47]	398.80 [47]	401.50 [47]	402.3 [47]	397.05 [43]		

* N5—pyrrole-like, N6—pyridine-like, and NG—graphite-like nitrogen; NP—pyridine oxide, N-Mo—molybdenum nitride.

Table 4. Fractions of different Mo species contributing integral intensities of Mo3d spectra obtained from the results of deconvolution of the high-resolution spectra of Mo3d.

Sample	MoO ₃ (5/2), %	MoO _x (5/2), %	MoO ₂ (5/2), %	MoN (5/2), %	
S1	48.33	4.87	33.32	13.48	
S2	58.34	24.16	15.30	2.17	

The analysis of the obtained results shows that the thickness of the nickel catalytic layer has a significant effect on the concentration of molybdenum nitride in Mo lower electrodes. Thus, the MoN concentration decreases from 13.48 to 2.17% with an increase in the thickness of the nickel catalytic layer from 5 to 15 nm (Table 4). This dependence is due to different probabilities of the formation of molybdenum oxide MoO_x and bonding with the catalytic layer in the form of MoNi₃ during the formation of catalytic centers at the stage of sample heating. So, the reaction with the formation of MoNi₃ is more likely to proceed at a thickness of Ni at 5 nm, and the process of oxidation of molybdenum with the

formation of MoO_x is more likely at a thickness of 15 nm. Further, during the growth of N-CNTs at the stages of activation and heating, the interaction of $MoNi_3$ with ammonia leads to the formation of molybdenum nitride, and the interaction of MoO_x with ammonia can gradually reduce the oxide to metallic molybdenum. In this case, the formation of molybdenum nitride leads to a redistribution of the ratio of the concentration of free carbon and nitrogen during the growth of N-CNTs. This fact leads to a redistribution of doped nitrogen between pyridine-, pyrrole-, and graphitic-like forms [33,35].

This statement is in agreement with the results of reconstructing the fine structure of the nitrogen line, which includes pyridine-, pyrrole-, and graphitic-like forms, pyridine oxide, and molybdenum nitride N-Mo (binding energies present in Table 3), based on separation of the photoelectronic signal of photoemission lines for N1s and Mo3p_{3/2}. Component analysis allowed us to calculate the areas under the curves related to the N1s photoelectronic signal (Table 5) and to obtain the refined values of the surface composition (Table 6).

Table 5. Parameters of deconvolution N1s/Mo3p_{3/2} spectra.

Components -		Sample S1, Al k	Κα (1486.6 eV)		Sample S2, Synchrotron Source (850 eV)					
	BE, eV	Peak Intensity	FWHM, eV	Peak Area	BE, eV	Peak Intensity	FWHM, eV	Peak Area		
MoO ₂ 3p(3/2)	395.02	2394.99	2.21	5739.58	394.5	502.41	1.68	874.7		
$MoO_3 3p(3/2)$	398.2	3877.06	1.98	8322.4	398.03	1809.46	1.61	3335.36		
$MoO_x 3p(3/2)$	395.92	350.09	2.21	838.98	396.2	794.27	1.68	1383.95		
NĜ	398.49	625.04	1.66	1124.25	399	634.57	1.44	992.73		
N5	399.81	1125.1	1.66	2023.69	399.79	1208.29	1.44	1890.25		
NG	400.81	756.54	1.66	1360.78	401.2	864.42	1.44	1352.3		
NP	402.2	365.61	1.86	657.61	402.85	221.56	1.64	346.38		
MoN 3p(3/2)	394.83	970.04	2.21	2324.69	393.4	119.07	1.53	124.21		
N-Mo	396.8	1239.85	1.66	2230.1	397.16	671.08	1.44	1049.84		

Table 6. Recalculated surface composition of the N-CNTs and nitrogen components of the samples.

Sample	C1s, %	O1s, %	Mo3d, %	N1s, %	N-Mo, %	N5, %	N6, %	NG, %	NP, %
S1	77.46	11.01	5.07	6.47	1.95	1.77	0.98	1.19	0.58
S2	81.43	9.33	3.33	5.91	0.77	2.05	1.22	1.46	0.42

The proportion of pyrrole-like nitrogen is 27% and of pyridine-like is 15% of the total nitrogen content in the N-CNTs of the S1 sample (Table 6). In the S2 sample, the concentration of pyrrole- and pyridine-like nitrogen increases to 35% and 20%, respectively. This dependence is due to the fact that the concentration of free nitrogen increases with a decrease in the formation of molybdenum nitrides, with an increase in the thickness of the nickel catalytic layer. As a result, the ratio of free nitrogen and carbon flows entering the surface of catalytic centers during the growth of N-CNTs increases. This fact leads to the predominant formation of pyrrole-like nitrogen [33]. The concentration of pyrrole-like nitrogen, in turn, determines the piezoelectric properties of N-CNTs [33–35].

The results of the AFM study of the samples showed an increase in the piezoelectric response of N-CNTs from 12 to 17 nA with an increase in pyrrole-like nitrogen from 1.77 to 2.05% (Figure 5a). As we have previously found, the generation of current during the deformation of N-CNTs is due to the formation of a surface potential as a result of the manifestation of the piezoelectric properties of N-CNTs [48]. The origin of the piezoelectric properties of N-CNTs are bamboo-like defects in the cavity of the nanotube (Figure 5b), which are a curved graphene sheet with a non-zero dipole moment due to curvature-induced polarization [49]. The total polarization of N-CNTs is the sum of the dipole moments of all bamboo-like defects per unit volume [34]. As a result, it is necessary to increase the number of bamboo-like defects, which is determined by the concentration of pyrrole-type nitrogen, to increase the piezoelectric response of N-CNTs [33]. Thus, the observed increase in the piezoelectric response for the S2 sample relative to the S1 sample is in agreement with the previously proposed mechanism of the piezoelectric effect in

N-CNTs, which is associated with the formation of bamboo-like defects as a result of the incorporation of pyrrole-like nitrogen [33].



Figure 5. (a) Piezoelectric response of the N-CNTs when an external force of 0 to 2 μ N is applied. The insert shows a schematic representation of the measurement process. (b) TEM image of bamboo-like defects in N-CNTs.

Thus, it has been shown that deconvolution of the high-resolution spectra of overlapping photoemission lines for N1s and $Mo3p_{3/2}$ makes it possible to efficiently restore the fine structure of the nitrogen line and separate the components of pyridine-, pyrrole-, and graphitic-like nitrogen and molybdenum nitride, both in the laboratory and the synchrotron XPS method. The obtained results allowed us to study the effect of the thickness of the nickel catalytic layer of the N-CNT samples on the concentration and the type of doping nitrogen and piezoelectric response. At the same time, the calculation of the element atom concentrations of the N-CNTs by determining the curve areas of the corresponding components and their normalization gives overestimated values of nitrogen concentration due to overlapping core lines of N1s and $Mo3p_{3/2}$ (Table 1).

In this way, the analysis of the high-resolution spectra and deconvolution results indicates that the interpretation of XPS results primarily depends on the sequence and algorithm used for calculating the fine structure. The overlapping N1s and $Mo3p_{3/2}$ photoelectron core lines lead to significant difficulties in peak fitting, which requires the development of guides in the analysis of multicomponent systems of the N-CNTs/Mo type by the XPS method. The described process in this study of interpreting XPS data makes it possible to avoid gross errors in the study of the surface composition and nitrogen components of the N-CNTs. It is shown that a correct analysis of XPS spectra provides very important information about the distribution of nitrogen over emerging defect types, which later determine the chemical and electrical properties of the N-CNTs.

4. Conclusions

In summary, we studied the composition and stoichiometry of a multicomponent system based on nitrogen-doped carbon nanotubes using the laboratory and synchrotron XPS methods. We used a general algorithm for analyzing and calculating the fine structure of the spectra when processing data obtained on the laboratory spectrometer and the XPS synchrotron source. Thus, we have shown that the resolution of the spectra obtained using a laboratory spectrometer is comparable to the results of synchrotron studies for the N-CNTs. However, a longer statistical signal accumulation is required to achieve comparable spectral resolution on standard laboratory equipment with a sufficient signal-to-noise ratio. Thus, the results presented in this paper indicate that the use of synchrotron and laboratory sources does not affect the error of the quantitative calculation for studying the composition

of multicomponent systems of the N-CNTs/Mo type using the XPS method. This allows for planning of the XPS experiment in detail to characterize the concentration and type of doping nitrogen in N-CNTs.

In addition, according to the results of deconvolution of the high-resolution spectra of the Mo3d core line, oxide and nitride layers are formed on the surface of molybdenum, corresponding to the compounds MoO_2 , MoO_x , MoO_3 , and MoN. The calculated concentration ratios of the molybdenum components made it possible to analyze the fine structure of the overlapping high-resolution spectra of the N1s and $Mo3p_{3/2}$ lines. It was found that the formed N-CNTs contain nitrogen chemically bonded to carbon with pyridine-, pyrrole-, and graphitic-like forms. Based on the results, the influence of the thickness of the nickel catalytic layer on the concentration of molybdenum nitride and the type of incorporation of doping nitrogen into N-CNTs was established. A direct relationship between the pyrrole-like nitrogen and the piezoelectric response of N-CNTs was shown. The obtained results should be taken into account when developing energy conversion and storage devices based on the N-CNTs.

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References

- Isaacs, M.A.; Davies-Jones, J.; Davies, P.R.; Guan, S.; Lee, R.; Morgan, D.J.; Palgrave, R. Advanced XPS Characterization: XPS-Based Multi-Technique Analyses for Comprehensive Understanding of Functional Materials. *Mater. Chem. Front.* 2021, 5,7931–7963. [CrossRef]
- Pagliara, P.; Chirizzi, D.; Guascito, M.R. Chemical Characterization of Red Cells from the Black Sea Urchin Arbacia Lixula by X-ray Photoelectron Spectroscopy. RSC Adv. 2021, 11, 27074–27083. [CrossRef]
- Shchukarev, A.; Backman, E.; Watts, S.; Salentinig, S.; Urban, C.F.; Ramstedt, M. Applying Cryo-X-ray Photoelectron Spectroscopy to Study the Surface Chemical Composition of Fungi and Viruses. *Front. Chem.* 2021, 9, 666853. [CrossRef] [PubMed]
- Andronowski, J.M.; Mundorff, A.Z.; Davis, R.A.; Price, E.W. Application of X-ray Photoelectron Spectroscopy to Examine Surface Chemistry of Cancellous Bone and Medullary Contents to Refine Bone Sample Selection for Nuclear DNA Analysis. *J. Anal.* Spectrom. 2019, 34, 2074–2082. [CrossRef]
- Chakraborty, D.; Sarkar, S.; Das, P.K. Blood Dots: Hemoglobin-Derived Carbon Dots as Hydrogen Peroxide Sensors and Pro-Drug Activators. ACS Sustain. Chem. Eng. 2018, 6, 4661–4670. [CrossRef]
- Wang, X.; Qin, X.; Wang, W.; Liu, Y.; Shi, X.; Sun, Y.; Liu, C.; Zhao, J.; Zhang, G.; Liu, H.; et al. Interface Chemistry and Surface Morphology Evolution Study for InAs/Al2O3 Stacks upon in Situ Ultrahigh Vacuum Annealing. *Appl. Surf. Sci.* 2018, 443, 567–574. [CrossRef]
- Feng, Z.; Peng, Y.; Liu, H.; Sun, Y.; Wang, Y.; Meng, M.; Liu, H.; Wang, J.; Wu, R.; Wang, X.; et al. The Band Structure Change of Hf0.5Zr0.5O2/Ge System upon Post Deposition Annealing. *Appl. Surf. Sci.* 2019, 488, 778–782. [CrossRef]
- Shi, X.; Wang, X.; Sun, Y.; Liu, C.; Wang, W.; Cheng, Y.; Wang, W.; Wang, J.; Cho, K.; Lu, F.; et al. Interface Chemistry Study of InSb/Al₂O₃ Stacks upon in Situ Post Deposition Annealing by Synchrotron Radiation Photoemission Spectroscopy. *Appl. Surf. Sci.* 2017, 425, 932–940. [CrossRef]
- Wagner, C.D.; Naumkin, A.V.; Kraut-Vass, A.; Allison, J.W.; Powell, C.J.; Rumble, R. NIST Standard Reference Database 20, Version 3.4 (Web Version); National Institute of Standards and Technology: Gaithersburg, MD, USA, 2003.

- Greczynski, G.; Hultman, L. X-ray Photoelectron Spectroscopy: Towards Reliable Binding Energy Referencing. *Prog. Mater. Sci.* 2020, 107, 100591. [CrossRef]
- Major, G.H.; Avval, T.G.; Moeini, B.; Pinto, G.; Shah, D.; Jain, V.; Carver, V.; Skinner, W.; Gengenbach, T.R.; Easton, C.D.; et al. Assessment of the Frequency and Nature of Erroneous X-ray Photoelectron Spectroscopy Analyses in the Scientific Literature. J. Vac. Sci. Technol. A 2020, 38, 061204. [CrossRef]
- Linford, M.R.; Smentkowski, V.S.; Grant, J.T.; Brundle, C.R.; Sherwood, P.M.A.; Biesinger, M.C.; Terry, J.; Artyushkova, K.; Herrera-Gómez, A.; Tougaard, S.; et al. Proliferation of Faulty Materials Data Analysis in the Literature. *Microsc. Microanal.* 2020, 26, 1–2. [CrossRef] [PubMed]
- Kalha, C.; Fernando, N.K.; Bhatt, P.; Johansson, F.O.L.; Lindblad, A.; Rensmo, H.; Medina, L.Z.; Lindblad, R.; Siol, S.; Jeurgens, L.P.H.; et al. Hard X-ray Photoelectron Spectroscopy: A Snapshot of the State-of-the-Art in 2020. *J. Phys. Condens. Matter* 2021, 33, 233001. [CrossRef]
- Murakami, R.; Kageyama, H.; Nakamura, K.; Tanaka, H.; Shinotsuka, H.; Yoshikawa, H.; Yoshihara, K. Background Estimation in X-ray Photoelectron Spectroscopy Data Using an Active Shirley Method with Automated Selection of the Analytical Range. *E-J. Surf. Sci. Nanotechnol.* 2019, 17, 61–68. [CrossRef]
- Siol, S.; Mann, J.; Newman, J.; Miyayama, T.; Watanabe, K.; Schmutz, P.; Cancellieri, C.; Jeurgens, L.P.H. Concepts for Chemical State Analysis at Constant Probing Depth by Lab-based XPS/HAXPES Combining Soft and Hard X-ray Sources. *Surf. Interface Anal.* 2020, 52, 802–810. [CrossRef]
- Major, G.H.; Fairley, N.; Sherwood, P.M.A.; Linford, M.R.; Terry, J.; Fernandez, V.; Artyushkova, K. Practical Guide for Curve Fitting in X-ray Photoelectron Spectroscopy. J. Vac. Sci. Technol. A 2020, 38, 061203. [CrossRef]
- Baer, D.R.; Artyushkova, K.; Richard Brundle, C.; Castle, J.E.; Engelhard, M.H.; Gaskell, K.J.; Grant, J.T.; Haasch, R.T.; Linford, M.R.; Powell, C.J.; et al. Practical Guides for X-ray Photoelectron Spectroscopy: First Steps in Planning, Conducting, and Reporting XPS Measurements. J. Vac. Sci. Technol. A 2019, 37, 031401. [CrossRef]
- Faisal, S.N.; Haque, E.; Noorbehesht, N.; Zhang, W.; Harris, A.T.; Church, T.L.; Minett, A.I. Pyridinic and Graphitic Nitrogen-Rich Graphene for High-Performance Supercapacitors and Metal-Free Bifunctional Electrocatalysts for ORR and OER. RSC Adv. 2017, 7, 17950–17958. [CrossRef]
- Bianco, A.; Chen, Y.; Frackowiak, E.; Holzinger, M.; Koratkar, N.; Meunier, V.; Mikhailovsky, S.; Strano, M.; Tascon, J.M.D.; Terrones, M. Carbon Science Perspective in 2020: Current Research and Future Challenges. *Carbon NY* 2020, 161, 373–391. [CrossRef]
- Arkhipova, E.A.; Ivanov, A.S.; Strokova, N.E.; Chernyak, S.A.; Shumyantsev, A.V.; Maslakov, K.I.; Savilov, S.V.; Lunin, V.V. Structural Evolution of Nitrogen-Doped Carbon Nanotubes: From Synthesis and Oxidation to Thermal Defunctionalization. *Carbon N. Y.* 2017, 125, 20–31. [CrossRef]
- 21. Bulyarskiy, S.V.; Bogdanova, D.A.; Gusarov, G.G.; Lakalin, A.V.; Pavlov, A.A.; Ryazanov, R.M. Nitrogen in Carbon Nanotubes. *Diam. Relat. Mater.* 2020, 109, 108042. [CrossRef]
- Yamada, Y.; Kim, J.; Matsuo, S.; Sato, S. Nitrogen-Containing Graphene Analyzed by X-ray Photoelectron Spectroscopy. *Carbon N. Y.* 2014, 70, 59–74. [CrossRef]
- Lee, W.J.; Maiti, U.N.; Lee, J.M.; Lim, J.; Han, T.H.; Kim, S.O. Nitrogen-Doped Carbon Nanotubes and Graphene Composite Structures for Energy and Catalytic Applications. *Chem. Commun.* 2014, 50, 6818–6830. [CrossRef] [PubMed]
- Podyacheva, O.Y.; Suboch, A.N.; Yashnik, S.A.; Salnikov, A.V.; Cherepanova, S.V.; Kibis, L.S.; Simenyuk, G.Y.; Romanenko, A.I.; Ismagilov, Z.R. Effect of Structure and Surface State of Nitrogen Doped Carbon Nanotubes on Their Functional and Catalytic Properties. J. Struct. Chem. 2021, 62, 771–781. [CrossRef]
- Li, X.; Zhou, J.; Zhang, J.; Li, M.; Bi, X.; Liu, T.; He, T.; Cheng, J.; Zhang, F.; Li, Y.; et al. Bamboo-Like Nitrogen-Doped Carbon Nanotube Forests as Durable Metal-Free Catalysts for Self-Powered Flexible Li–CO₂ Batteries. *Adv. Mater.* 2019, *31*, 1901997. [CrossRef]
- Aoki, K.; Senga, R.; Suga, Y.; Totani, K.; Maki, T.; Itoh, H.; Shinokura, K.; Suenaga, K.; Watanabe, T. Structural Analysis and Oxygen Reduction Reaction Activity in Bamboo-like Nitrogen-Doped Carbon Nanotubes Containing Localized Nitrogen in Nodal Regions. *Carbon* 2017, 123, 99–105. [CrossRef]
- Sánchez-Salas, R.; Kashina, S.; Galindo, R.; Cuentas-Gallegos, A.K.; Rayón-López, N.; Miranda-Hernández, M.; Fuentes-Ramírez, R.; López-Urías, F.; Muñoz-Sandoval, E. Effect of Pyrrolic-N Defects on the Capacitance and Magnetization of Nitrogen-Doped Multiwalled Carbon Nanotubes. *Carbon N.Y.* 2021, 183, 743–762. [CrossRef]
- Ombaka, L.M.; Ndungu, P.G.; Nyamori, V.O. Pyrrolic Nitrogen-Doped Carbon Nanotubes: Physicochemical Properties, Interactions with Pd and Their Role in the Selective Hydrogenation of Nitrobenzophenone. RSC Adv. 2015, 5, 109–122. [CrossRef]
- Liang, L.; Xiao, M.; Zhu, J.; Ge, J.; Liu, C.; Xing, W. Low-Temperature Synthesis of Nitrogen Doped Carbon Nanotubes as Promising Catalyst Support for Methanol Oxidation. *J. Energy Chem.* 2019, 28, 118–122. [CrossRef]
- Zhu, S.; Dong, X.; Huang, H.; Qi, M. Rich Nitrogen-Doped Carbon on Carbon Nanotubes for High-Performance Sodium-Ion Supercapacitors. J. Power Sources 2020, 459, 228104. [CrossRef]
- Sumpter, B.G.; Meunier, V.; Romo-Herrera, J.M.; Cruz-Silva, E.; Cullen, D.A.; Terrones, H.; Smith, D.J.; Terrones, M. Nitrogen-Mediated Carbon Nanotube Growth: Diameter Reduction, Metallicity, Bundle Dispersability, and Bamboo-like Structure Formation. ACS Nano 2007, 1, 369–375. [CrossRef] [PubMed]

- 32. Louchev, O.A. Formation Mechanism of Pentagonal Defects and Bamboo-like Structures in Carbon Nanotube Growth Mediated by Surface Diffusion. *Phys. Status Solidi A Appl. Res.* **2002**, *193*, 585–596. [CrossRef]
- Il'ina, M.V.; Il'in, O.I.; Guryanov, A.V.; Osotova, O.I.; Blinov, Y.F.; Fedotov, A.A.; Ageev, O.A. Anomalous Piezoelectricity and Conductivity in Aligned Carbon Nanotubes. J. Mater. Chem. C Mater. 2021, 9, 6014–6021. [CrossRef]
- Il'ina, M.; Il'in, O.; Osotova, O.; Khubezhov, S.; Rudyk, N.; Pankov, I.; Fedotov, A.; Ageev, O. Pyrrole-like Defects as Origin of Piezoelectric Effect in Nitrogen-Doped Carbon Nanotubes. *Carbon* 2022, 190, 348–358. [CrossRef]
- Il'ina, M.V.; Soboleva, O.I.; Khubezov, S.A.; Smirnov, V.A.; Il'in, O.I. Study of Nitrogen-Doped Carbon Nanotubes for Creation of Piezoelectric Nanogenerator. J. Low Power Electron. Appl. 2023, 13, 11. [CrossRef]
- 36. Il'ina, M.V.; Osotova, O.I.; Rudyk, N.N.; Khubezhov, S.A.; Pankov, I.V.; Ageev, O.A.; Il'in, O.I. Sublayer Material as a Critical Factor of Piezoelectric Response in Nitrogen-Doped Carbon Nanotubes. *Diam. Relat. Mater.* **2022**, *126*, 109069. [CrossRef]
- Molodtsov, S.L.; Fedoseenko, S.I.; Vyalikh, D.V.; Iossifov, I.E.; Follath, R.; Gorovikov, S.A.; Brzhezinskaya, M.M.; Dedkov, Y.S.; Püttner, R.; Schmidt, J.-S.; et al. High-Resolution Russian–German Beamline at BESSY. *Appl. Phys. A* 2009, *94*, 501–505. [CrossRef]
- Scofield, J.H. Hartree-Slater Subshell Photoionization Cross-Sections at 1254 and 1487 EV. J. Electron. Spectrosc. Relat. Phenom. 1976, 8, 129–137. [CrossRef]
- 39. Seah, M.P. Calibration of electron spectrometer energy scales for AES and XPS. J. Surf. Anal. 2022, 28, S30–S32. [CrossRef]
- 40. Tanuma, S.; Powell, C.J.; Penn, D.R. Calculations of Electron Inelastic Mean Free Paths. V. Data for 14 Organic Compounds over the 50–2000 EV Range. *Surf. Interface Anal.* **1994**, *21*, 165–176. [CrossRef]
- 41. Grosvenor, A.P.; Biesinger, M.C.; Smart, R.S.C.; McIntyre, N.S. New Interpretations of XPS Spectra of Nickel Metal and Oxides. *Surf. Sci.* 2006, 600, 1771–1779. [CrossRef]
- Yeh, J.J.; Lindau, I. Atomic Subshell Photoionization Cross Sections and Asymmetry Parameters: 1 ≤ Z ≤ 103. *Data Nucl. Data Tables* 1985, 32, 1–55. [CrossRef]
- 43. Sanjinés, R.; Wiemer, C.; Almeida, J.; Lévy, F. Valence Band Photoemission Study of the Ti-Mo-N System. *Thin Solid Film.* **1996**, 290–291, 334–338. [CrossRef]
- 44. Schrader, G. In Situ Laser Raman Spectroscopy of the Sulfiding of Mo/Al₂O₃ Catalysts. J. Catal. 1983, 80, 369–385. [CrossRef]
- Anwar, M.; Hogarth, C.A.; Bulpett, R. An XPS Study of Amorphous MoO₃/SiO Films Deposited by Co-Evaporation. J. Mater. Sci. 1990, 25, 1784–1788. [CrossRef]
- 46. Okamoto, Y. Surface Structure and Catalytic Activity of Sulfided MoO₃/Al₂O₃ Catalysts: Hydrodesulfurization and Hydrogenation Activities. *J. Catal.* **1980**, *66*, 93–100. [CrossRef]
- 47. Bianco, G.V.; Sacchetti, A.; Grande, M.; D'Orazio, A.; Milella, A.; Bruno, G. Effective Hole Conductivity in Nitrogen-Doped CVD-Graphene by Singlet Oxygen Treatment under Photoactivation Conditions. *Sci. Rep.* **2022**, *12*, 8703. [CrossRef]
- Il'ina, M.; Il'in, O.; Blinov, Y.; Konshin, A.; Konoplev, B.; Ageev, O. Piezoelectric Response of Multi-Walled Carbon Nanotubes. *Materials* 2018, 11, 638. [CrossRef]
- 49. Kundalwal, S.I.; Meguid, S.A.; Weng, G.J. Strain Gradient Polarization in Graphene. Carbon 2017, 117, 462–472. [CrossRef]

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