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Sami Sainio,* Niklas Wester, Anja Aarva, Charles J. Titus, Dennis Nordlund, Esko I. Kauppinen, Elli Leppänen, Tommi Palomäki, Jessica E. Koehne, Olli Pitkänen, Kristzian Kordas, Maria Kim, Harri Lipsanen, Miran Mozetič, Miguel A. Caro, M. Meyyappan, Jari Koskinen, and Tomi Laurila

ABSTRACT: Successful deployment of carbon nanomaterials in many applications, such as sensing, energy storage, and catalysis, relies on the selection, synthesis, and tailoring of the surface properties. Predictive analysis of the behavior is difficult without detailed knowledge of the differences between various carbon nanomaterials and their surface functionalization, thus leaving the selection process to traditional trial-and-error work. The present characterization fills this knowledge gap for carbon nanomaterial surface properties with respect to chemical states and functionalization. We present an overview of the chemical trends that can be extracted from soft X-ray absorption spectroscopy (XAS) spectra on an extended set of nonideal carbon nanomaterials as a function of sp² bonded carbon and bond ordering. In particular, the surface chemical state, the presence of long-range order in the carbon matrix, and a qualitative estimation of the amount of oxygen and nitrogen and their respective functional group formation on the material surface, together with the detailed material fabrication parameters, are reported. The results expand our understanding of carbon nanomaterial functionalization, which can support material selection in practice, provided that the specifications of the application are known.

INTRODUCTION

Carbon nanomaterials (CNMs) are used in a wide range of applications, including sensors,1–4 energy storage and conversion,5,6 catalysis,7 advanced composites,8 drug delivery platforms,9 and many more. They are also used in several industrial applications as wear-protective coatings for disk-drive read head coating using a diamond-like carbon,10 touch panels with conductive carbon nanotubes (CNTs)11 and graphene,12 conductive additives in electrode materials for batteries, additives in anticorrosion primers, precursors for thermal dissipation films,12 and anode materials in lithium-ion batteries,13 to name a few examples. The surface chemistry plays a key role in the sensitivity and selectivity of sensors,14 surface wettability,15 covalent binding of enzymes and antibodies,16 cell viability,17 and tribological properties.18 To broaden the applicability of these often quite unideal carbon nanomaterials into new industrial-scale applications, it is crucial to develop a mechanistic understanding of their surface chemistry (or a better understanding of the functionality of their surface chemistry). As shown in ref 19, there is a serious lack of (i) systematic characterization of carbon nanomaterials and (ii) standardized protocols for characterizing the surface functional groups of carbon nanomaterials. Furthermore, most past studies do not explicitly state how the studied materials were grown or prepared, and in some cases, only the vendor information is available. Thus, our ability to tailor carbonaceous nanomaterials for specific applications is limited. Here, we provide details of the fabrication process for a wide range of extensively used carbon nanomaterials, as well as the results of X-ray absorption spectroscopy (XAS) analysis, to be able to provide a consistent and systematically constructed dataset, which allows for more robust extraction of trends. Note that this paper is intended to provide information about the overall trends that can be seen in these often nonideal carbon nanomaterials used in the actual applications. Similar approaches can be found for conjugated polymers,20 carbon-yl-containing polymers,21 asphaltenies,22 polycyclic aromatic hydrocarbons,23 natural organic carbon,24 soil organic carbon,25 a wide array of molecular carbon compounds in various groupings,26 to name a few. This paper is not intended to be an in-depth investigation of the detailed surface chemical properties of a single ideal carbon allotrope that would be targeted solely for research purposes. The latter can...
<table>
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<tr>
<th>Material</th>
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<th>Method</th>
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<tr>
<td>DND</td>
<td>Si + DND (single digit, crystal size 4−6 nm)</td>
<td>Drop casting</td>
<td>NA</td>
<td>Dilution of 5 wt %, andante DND water suspension to 0.05 wt % with DI water; drop cast 60 μL on Si and dried at room temp.</td>
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<td>Carbodeon Ltd., Finland</td>
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<tr>
<td>ta-C</td>
<td>Si + 20 nm Ti + 7 nm ta-C Ti: DC-MS 2 in. Ti target (99.995%, Kurt J. Lesker)</td>
<td>Ti: 100 W, 30 sccm Ar (5 mTorr), 350 s, 17 rpm sample rotation</td>
<td>57</td>
<td>ta-C: p-FCVA graphite rod (99.95%, Graphite Store) C: 400 V, 550 pulses, 1 Hz, &lt;10−6 Torr, 17 rpm sample rotation</td>
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<tr>
<td>a-C</td>
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<td>2000 W, pulsed DC mode (100 kHz), 80 sccm Ar (3 mTorr)</td>
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<td>a-C: p-FCVA graphite powder (&lt;20 μM, Sigma-Aldrich, product number: 282863) drop cast 60 μL water suspension on Si wafer (0.1 g/100 mL) and dried at room temp</td>
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<td>GO</td>
<td>Si + GO modified Hummers' method; drop casting graphite powder (&lt;20 μM, Sigma-Aldrich, product number: 282863)</td>
<td>Drop casting</td>
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<td>GO: PECVD C 2H2,N H 3 CNF: pre-anneal 3 min, 400 °C, &lt;1 Pa, 600 °C (300 °C/min), 150 W DC plasma, 30 sccm C 2H2, 125 sccm NH3, 30 min</td>
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<td>Si + 20 nm Ti + 7 nm ta-C + 20 nm Fe (forest-like orientation, 20−80 nm wide, 200−350 nm tall)</td>
<td>Ti: DC-MS 2 in. Ti target (99.995%, Kurt J. Lesker) Ti: arc current 55 A, 40 s, sample rotation 2.1 rpm</td>
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<td>Si + 20 nm Ti + 15 nm ta-C + 0.2 nm Al + 2 nm Fe + 2 nm Co (tangled, spaghetti-like orientation, 20−40 nm wide, up to 10 μm long)</td>
<td>Ti: continuous current arc</td>
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<td>Al, Fe: RF-MS 2 in. Al target (99.99%, Kurt J. Lesker); 2 in. Fe target (99.9%, Kurt J. Lesker); Co pellets (99.9%, Kurt J. Lesker) Al: RF-MS, 33 W, 2.4 mTorr Ar, 0.1 Å/s, 65 s; Fe: RF-MS, 63 W, 2.4 mTorr Ar, 0.2−0.4 Å/s, 70 s; Co: thermal evaporation, 222 A, 1.8 V, 0.2−0.4 Å/s, 65 s</td>
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<td>Si + SWCNT (tangled, spaghetti-like orientation, 1.5−2.1 nm wide, 1−10 μm long)</td>
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<tr>
<td>CNW</td>
<td>Si PECVD pyrolytic graphite (99.9%)</td>
<td>800 °C, inductively coupled plasma (ICP) 500 W sustained at 30 mTorr, 200 s, 0.22 Torr at flowing in CO 2, 1 min</td>
<td>62 and 65</td>
<td>CNW: CVD 100 °C, 5 min</td>
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*a The processes are described in more detail in the references.*
be found in multiple publications, e.g., for graphene,\textsuperscript{32–34} carbon nanotubes,\textsuperscript{32–34} graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}),\textsuperscript{35} C60/ C70,\textsuperscript{36} diamond,\textsuperscript{37} nanodiamonds (NDs),\textsuperscript{38} and amorphous carbon (a-C).\textsuperscript{39} An interesting one-dimensional carbon allotrope carbyme was also proposed for the first time already in 1967\textsuperscript{40} and further studied more recently.\textsuperscript{41,42} However, as it is, at the present stage, not utilized extensively in any widespread applications in contrast to the other carbon allotropes as well as due to the lack of appropriate material sample, carbyme is not included in the material portfolio of this study and will not be discussed further.

In the field of electrochemical applications, there is a long-standing debate regarding which properties of carbon nanomaterials are the most critical in determining their electrocatalytic performance. One of the common hypotheses claims that the edge planes are more active than the basal planes in carbon nanomaterials when they are both present.\textsuperscript{43,44} Numerous publications also show possible connections between the amount of the sp\textsuperscript{2}/sp\textsuperscript{3} fraction and the surface oxygen content.\textsuperscript{45–48} In addition to the total oxygen content, the types of functional groups present on the surface as well as species dissolved subsurface have been observed to affect the electrocatalytic properties.\textsuperscript{49} Thus, to understand the performance of a given carbon nanomaterial in a specific application, such as those listed above, functional groups and other physicochemical features of the surface must be known accurately. It must be noted that it has also been speculated that the residual catalyst metals may in fact have a dominating effect on the electrochemical properties of carbonaceous nanomaterials, although there also exist arguments against this claim, especially when considering the effects of additives combined with graphene.\textsuperscript{50} While this work focuses on the chemistry of carbon nanomaterials, disregarding the presence of trace metals, we acknowledge that the metal catalysts used in many of the fabrication processes of the carbon nanomaterials are also likely to play a significant role in their performance in various applications. Detailed analysis of the amount of trace elements and their chemical states for the current set of carbon materials will be considered in our future work. Hence, our primary goal here is to provide a chemical and structural map that can be used to navigate through the rich landscape of carbon nanomaterials used in practical applications.

## EXPERIMENTAL SECTION

### Material Fabrication.

Highly ordered pyrolytic graphite (HOPG) was acquired from Scanwel (see Table 1 for details). To expose a fresh surface, a scotch tape method\textsuperscript{49} was used to peel several layers off from the HOPG prior to measurement. Single-digit detonation nanodiamond (DND) in a solution with a potential of +40 mV prepared from detonation soot and chemically purified to remove the sp\textsuperscript{2} carbon and metal impurities was obtained from Carbodeon. All other materials were deposited specifically for this work. The carbon nanomaterials in water solution were drop cast onto borondoped (100) Si wafers (resistance <0.005 Ω·cm). Graphite oxide (GO) was synthesized from synthetic graphite powder (Sigma-Aldrich) following a modified Hummers’ method\textsuperscript{50,51} and exfoliated into GO by sonication as described in ref 52. The suspension was dried after sonication to obtain GO powder that was further dispersed in deionized (DI) water to achieve a solution with 0.1 g/100 mL. A 60 μL drop of this solution was then drop cast on a Si substrate and dried overnight. A 200 nm thick a-C layer was deposited by closed-field unbalanced magnetron sputtering (CFUBMS) as described in refs 53 and 54. Seven nanometer thick tetrahedral a-C (ta-C) samples were deposited using a pulsed filtered cathodic vacuum arc (p-FCVA). A 20 nm Ti adhesion layer first was deposited by direct current magnetron sputtering (DC-MS). The other CNMs discussed in this study were grown by chemical vapor deposition (CVD) or plasma-enhanced chemical vapor deposition (PECVD). Prior to CNM growth, the adhesion and metal catalyst layers were deposited either with a continuous current arc, p-FCVA, radio frequency magnetron sputtering (RF-MS), or thermal evaporation. Further details can be found in Table 1.

Carbon nanofiber (CNF), and multi-wall carbon nanotube (MWCNT) were grown directly on Si wafers from physical vapor deposition (PVD) predeposited catalyst layers. Carbon nanowall (CNW) samples were grown from pyrolytic graphite placed on top of the Si substrate. Graphene\textsubscript{CVD} was grown on copper foil and transferred to a Si wafer by first spin-coating poly(methyl methacrylate) (PMMA) onto the graphene/Cu film. An aqueous solution of NaOH was employed for electrochemical delamination (bulking transfer) as an electrolyte, while Cu was polarized at −3 V to delaminate PMMA/graphene. Then, PMMA/graphene was picked up by a carrier wafer to deionized water and transferred onto Si wafers, which were cleaned beforehand in acetone + ultrasonication for 5 min and rinsed in isopropyl alcohol.

Graphene\textsubscript{HT} films were grown by annealing the Si face of 4-H SiC substrates at atmospheric pressure in Ar ambient at 1650 °C for 3 min. Atomic force microscopy (AFM) measurements show a surface structure with a periodical terrace characteristic to graphene layers. The height of the terraces was around 0.5 nm. The thickness and quality of the film were estimated by means of Auger and Raman spectroscopy that confirmed the presence of a single layer of graphene and low defect density in the graphene film before patterning. According to Auger measurements, the total coverage of the SiC surface by graphene was a bit less than 1. Indicating that the growth process was terminated before the second graphene layer started to grow.\textsuperscript{55}

Single-wall carbon nanotube (SWCNTs) were synthesized by aerosol CVD and collected on nitrocellulose filters. The graphene and SWCNTs were press-transferred on Si substrates. More detailed descriptions of the deposition processes can be found based on the references given in Table 1.

### Data Collection, Preparation, and Peak Fitting.

XAS measurements were carried out at the Stanford Synchrotron Radiation Lightsource (SSRL) bending magnet beamline 8–2 at a 55° incidence angle (magic angle) of X-ray incidence. Beamline 8–2 is equipped with a spherical grating monochromator, operated using 40 × 40 μm\textsuperscript{2} slits, resulting in a resolution of around 200 meV. The spot size at the interaction point was around 1 × 1 mm\textsuperscript{2} and the total flux was in the order of 10\textsuperscript{18} photons/s for which beam damage was not noticeable even for extended exposure. The X-ray energy for the carbon 1s, nitrogen 1s, and oxygen 1s edges were scanned from 260 to 350, 380 to 430, and 520 to 560 eV, respectively. The data were collected both in the total electron yield (TEY) and Auger electron yield (AEY) modes using the drain current (amplified by a Keithley picoammeter) and a cylindrical mirror analyzer (CMA) operated with a pass energy of 200 eV and set to record the main Auger line for the various edges, respectively. The incoming flux was recorded using a nickel
grid with a Au sputtered film (called the i0). The data collected using the i0 follows the same procedure as the TEY measurements mentioned above. See Figure S1 for i0 spectra for C 1s, O 1s, and N 1s edges. For details on how to carefully plan XAS measurements and for general information about the measurements, we refer the reader to refs 64–66.

The data were normalized as follows. The slope of the linear background (initially fitted to the pre-edge region) was allowed to vary within a small range to keep both the area and edge jump constant across the dataset. The theoretical underpinning of edge jump normalization is well established (textbook normalization) and represents the atomic cross-section for the

![Graphical representation](https://dx.doi.org/10.1021/acs.jpcc.0c08597
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Figure 1. Trends in C 1s, O 1s, and N 1s XAS of 12 different carbon nanomaterials accompanied by highly ordered pyrolytic graphite (HOPG). Left is the C 1s normalized spectra (red), next on the right is O 1s normalized spectra (blue), center is O 1s absolute intensity spectra (blue dashed), next on the right N 1s normalized intensity (green), and on the right N 1s absolute intensity (green dashed). Peak positions are marked in the top legend and numbered and dashed lines drawn to the position of the expected peak positions to the spectra to guide the eye. Key for abbreviations: single-wall carbon nanotube (SWCNT), carbon nanowall (CNW), multi-wall carbon nanotube (MWCNT), carbon nanofiber (CNF), graphene oxide (GO), amorphous carbon (a-C), tetrahedral amorphous carbon (ta-C), and detonation nanodiamond (DND). Absolute intensity refers to the intensity that has not been normalized, meaning that the spectra have been background corrected and energy calibrated, but its intensity is as measured. Note that HOPG-normalized O 1s intensity features are likely caused by the normalization error as the absolute intensity is featureless.
atom, which is independent of the chemical surrounding (when done at high enough energy above the edge). The area normalization is based on the sum rules that associate the X-ray absorption total cross-section with the density of unoccupied 2p states (in the case of a 1s absorption even under dipole conditions). By forcing both the edge jump and the area to be the same, we are making the assumption that the difference in unoccupied 2p states between the spectra is not varying, which is strictly not true when looking at different chemical environments. However, in practice, the knowledge about the exact background function to use in the textbook normalization (which is presumed in the edge jump) in the soft X-ray regime is in many cases weak, at best, and in many cases erroneous, resulting in wide variations in normalization across similar samples depending on the signal to background and other experimental conditions, a highly undesirable condition. Making use of a stricter normalization rule such as keeping the area and edge jump constant will result in a very robust collective dataset that can be used with much higher confidence to look at small variations between similar samples, and it avoids experimental conditions and normalization artifacts to play a significant role in the analysis. Moreover, it provides a transparent way of comparing spectra across studies. Thus, we have applied this method here.

The data was prepared for publication using IGOR 8.06 software. Prior to the peak fitting procedure, the data was energy corrected and aligned using a Gaussian peak fit to the C 1s sp$^2$ $\pi^*$ feature of the reference sample and shifting all data accordingly to match the C 1s sp$^2$ $\pi^*$ at 285.2 eV. Furthermore, C 1s, O 1s, and N 1s regions were area normalized over the $\sigma$ and $\pi$ regions. Area normalization was performed (energy ranges of 280–320, 395–425, and 527–547 eV was set to have an area of 20) to enable comparison of relative intensities within the dataset.

A custom peak fitting procedure was developed using asymmetric Gaussian functions for sharper features corresponding to bonded states below the ionization potential (IP), broader asymmetric line-shapes that captures sigma states, two ionization potentials, and a smoothed background HOPG signal to capture sp$^2$-like carbon (see Figure S2 in the Supporting Information for more details). All of the Gaussian functions representing different functional groups were assigned to have a maximum full width at half-maximum (FWHM) of 0.9 to attempt to capture specific locations of functional groups in the energy regime. Prior to fitting, the energy range in the C 1s was given variable weight, 1 for 280–283.2 and 292.25–309.2 eV, 5 for 283.25–292.2, and 0.1 for 309.25–320 eV. The motivation for these choices is discussed in the Results and Discussion section.

The data displayed in Figures 2 and 3 show a clear shift in the C 1s sp$^2$ $\pi^*$ energy, which is considered in detail in the next section. The energy calibration from the reference sample dip was further confirmed by carefully observing the alignment of the excitonic signature at 291.65 eV (which matches the literature value of 291.65 eV$^{66–68,70}$ very well), where present. If the excitonic feature was not visible (which is a strong indication of the material’s lack of long-range order), the carboxyl reference value was used at 288.63 eV, as the carboxyl feature is stable and well defined in energy, as proven both computationally$^{69}$ and experimentally.$^{71}$ The reference spectra for sp$^3$ contribution were aligned to match the second order bandgap of the diamond at 302.5 eV, which is clearly present in both the extracted literature reference spectra and the DND sample (see Figure S3).

The exciton in this study refers to graphitic (sp$^2$) exciton at energy 291.65 eV$^{66–68,70}$ and it should not be mixed with diamond (sp$^3$) bulk exciton at energy 289,30 eV$^{77,71}$ or with the $\sigma^*$ transition, near 292.3–293.0 eV$^{66,70,72–74}$ Additionally, the long-range order description of this exciton is used interchangeably with the excitonic signature as it describes the degree of order in the sp$^2$ matrix. As can be clearly seen in Figure 1 left column where C 1s spectra for the carbon nanomaterials are shown, the amount of sp$^2$ bonding (the intensity of the sp$^2$ peak at 285.20 eV) does not correlate with the excitonic feature at 291.65 eV. However, there is a marked correlation between the position and shape of the sp$^2$ $\pi^*$ peak and the appearance of the excitonic feature, as discussed in the Results and Discussion section.

As the exciton is not a chemical state, it is not driven by the changes in the local density of states (DOS) around the excited site. The carbon network allows the excitonic feature to form in the core–hole state and does not have a direct correspondence with the DOS. It is true that there is some directionality of the excitonic feature that makes it better visible at a higher incidence angle, but it does not broaden under any circumstances. Chemical states, in particular $\sigma$-like states and bands, will be shifted in energy due to a spread of carbon–carbon distances that occur with the increased amount of disorder. Disorder, resulting in broader sigma bands and states, is correlated with the disappearance of the exciton, but the exciton does not change in energy and width, reflecting the different characteristics of the exciton and sigma features. Generally, states in the $\pi^*$ region are more stable in energy since they are primarily driven by the local coordination, and the states are also not protruding far out from the excitation center making them less likely to rehybridize in the presence of second and third shell changes. Some states with a particularly local character, such as the carbonyl $\pi^*$ in the carboxyl group, are almost unaffected by the surrounding disorder.

**Computational Studies.** Computational methods offer new opportunities for studying and interpreting the experimental results. Computational ab initio references are free from the bias and controversy present in the literature references. The accuracy of the method depends on the level of theory that is used as well as the size of the dataset. Three total energy calculations are needed to obtain the spectra: two to find the right energy alignment and one to obtain the shape of the spectrum. In addition, the geometry and the electronic structure of the models have to be relaxed. The results presented here consist of hundreds of spectra (548 exactly), and the depicted spectra (Figure 2) are the average over all of the sites in the structures (Figure 3). In this case, the computational results seem to be in good agreement with experimental interpretation. The simulations were carried out at the density functional theory (DFT) level by utilizing the GPAW code.$^{75,76}$ The functional that was used was Perdew–Burke–Ernzerhof (PBE),$^{77}$ and van der Waals corrections were included.$^{78}$ Calculations were performed under periodic boundary conditions. Further details of the computational method can be found in refs 69 and 79–81.

**RESULTS AND DISCUSSION**

In the following, we will discuss the soft x-ray spectroscopy results originating from the total electron yield (TEY) spectra unless otherwise specified. The spectra shown in Figure 1

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reveal the C 1s normalized intensities and for O 1s and N 1s, both their absolute (where absolute intensity refers to the intensity that has not been area normalized but is shown as measured with i0 normalization) and normalized intensities (all materials were fabricated for this study, see Table 1 in the Experimental Section for details). Based on the C 1s, O 1s, and N 1s spectra shown in Figure 1, it is clear that all carbon nanomaterials studied have some oxygen contamination. The only material that appears nearly oxygen free is the highly ordered pyrolytic graphite (HOPG) reference sample as its C 1s spectra have peaks only at the well-established chemical shifts for a number of different carbonyl groups, which are well assigned and will be discussed later.

We have concentrated our O 1s analysis efforts within the π region (below ∼535 eV) as the intensities observed in the σ region could be arising from native oxide present at the Si wafer surface, which was used as a substrate for all of the carbon nanomaterials in this study. Based on the full dataset, the degree of the surface oxygen contamination changes drastically among the various carbon allotropes. Based on the TEY spectra, the most oxygen-rich surface is observed on tetrahedral amorphous carbon (ta-C) + Fe grown carbon nanofibers (CNFs), whereas the least amount of oxygen is observed on high temperature (HT) grown graphene (except for the reference HOPG, which has nearly no oxygen). These results are consistent with the more surface-sensitive Auger electron yield (AEY) study, which indicates strong agreement with the findings from the TEY study.

In our earlier work, we fitted the C 1s region with the following peaks: sp2 π*, C−OH, ketone/aldehyde groups, carboxyl, (Rydberg states just below the ionization potential (IP)) and the long-range order (sp2 core exciton). With this large dataset, it was not feasible to find transferrable fitting parameters, i.e., peak positions that can be used to fit the spectra of all of the materials, without significant peak travel (over ±300 meV). Thus, additional peaks were fitted between the sp2 π* and the exciton peaks to match the observed intensity. Furthermore, it is of high importance to note that the energy assignments of the carbon−oxygen functional groups in this work are approximations and are used to investigate trends in this dataset. Additionally, due to the differences in the properties of the carbon matrix between different samples, the sp2 π* peak has been allowed to float at 285.25 ± 0.15 eV. To capture the differences between materials that have well-defined and sharp sp2 π* transition and those with a broader sp2 π* feature, an additional peak was added to capture this intensity. This peak has been placed at 284.3 ± 0.1 eV. The positions for each functional group have been taken from the literature. We acknowledge that the oxygen functional group assignment shows poor agreement across many publications in material science. The most consistent information can be found from the electron energy loss spectroscopy (EELS) studies of molecular compounds measured by Hitchcock and co-workers and as well as for carboxyl groups, which are well assigned and will be discussed later. Our logic for peak assignments follows closely that of Urquhart and Ade (and citing work) in which chemical shifts for a number of different carbonyl groups were addressed systematically. For functional groups that are not readily available from simple molecular compounds, there is an inherent difficulty to assign spectral features and reliable unbiased energy assignment is difficult to obtain. Thus, using computational data to support the selection of peak positions would be extremely helpful. For carbon nanomaterials, this issue has been tackled in a recent work by Aarva et al., where the features present in the C 1s spectra of amorphous carbon thin films have been calculated from individual structural fingerprints where computationally generated structural models were sampled. However, there are computational studies that do not directly support our findings, such as Hunt et al. Especially when the matrix is

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**Figure 2.** Origin of the broadening of sp2 π* and other features of the spectra explained by utilizing density functional theory (DFT) simulations. Pristine graphene displays the same trend as HOPG, where there are no peaks indicating the presence of oxygen between the sp2 π* peak and the σ* peaks. The numbering used here for the spectral features is the same as used in Figure 1.

**Figure 3.** Structures that were used in simulations: (a) pristine graphene, (b) graphene with a single vacancy, and (c) graphene with oxygen-containing groups. The oxygen-containing structure (c) has been originally published in ref 113.
complex, traditional peak fitting schemes are quite inadequate for capturing all of the spectral features from functional groups, and its feasibility is thus inherently limited for many carbon nanomaterials. Finally, the sp\(^2\) and sp\(^3\) ratios for each material were extracted using a smoothed HOPG reference as a material to describe the sp\(^2\) contribution (which is discussed in more detail below) and the CVD grown sp\(^3\) containing films\(^94\)–\(^96\) as the measure of sp\(^3\) bonding. These CVD-grown films were grown in a hydrogen environment, and we selected the “H-450 W” from Coffman et al. work as the most representative for describing the sp\(^3\) bonding in materials of this study. This is due to the fact that the sharp diamond exciton observed at 289.3 eV in the literature\(^71,87,94\) is absent from all materials investigated in this study, including also the ones that are most likely to exhibit a significant amount of sp\(^3\)-bonded carbon, namely, in tetrahedral amorphous carbon (ta-C) and detonation nanodiamond (DND) samples, as can be seen from Figure 1 (see also Figure S3 for comparison of ta-C and DND with the H-450 W reference spectra). The proposed method to extract the sp\(^2\) and sp\(^3\) ratios does not take into account that (i) some of the intensities at peaks at 284.34 and 285.2 eV are likely arising from the sp\(^2\)-carbon and (ii) the sp\(^3\) background does not capture all sp\(^2\)-bonded carbon, especially in the case of amorphous diamond-like carbon (ta-C and possibly to some degree also a-C like samples). The literature has some authoritative work, e.g., ref 71 and 94, studying how the changes in the carbon matrix (sp\(^2\) vs sp\(^3\)) changes their representative XAS spectra, but there is no fitting procedure proposed. There are some publications about the fitting procedure for extracting the sp\(^2\) ratio using the sp\(^2\) π\(^*\) peak and integrating over the energy range to capture the sp\(^3\) σ\(^*\) intensity,\(^97\) but a clear debate exists on the selection of the appropriate σ\(^*\) energy range.\(^98\)–\(^101\) Additionally, not all of the observed changes in the spectra have been strongly connected to the structural changes; therefore, the differences between the carbon matrix containing crystalline, partially crystalline, and amorphous sp\(^3\) carbon are hard to compare with respect to their sp\(^3\) content. This calls for further experimental and computational work to produce strong fingerprints for both amorphous and crystalline sp\(^3\) materials with and without oxygen contaminants. Thus, there are clear similarities in ta-C and a-C spectra (see Figure 1), but the fit suggests that there is no sp\(^3\) in a-C, and the result needs to be critically evaluated.

In principle, computational tools can provide a new route toward establishing more robust links between the atomic motifs present in the materials and the corresponding spectral features found on their X-ray spectra. The accuracy of these tools can be validated against molecular refs\(^102\)–\(^104\) and ideal extended structures (e.g., graphene, HOPG, and diamond), and then used to accurately predict and interpret the experimental spectra of more complex materials.\(^69,92\) For instance, computationally, one can establish a one-to-one correspondence between each of the functional groups present on a material and their contribution to the spectra throughout the full range of scanned energies. However, since the required and reliable computational structural models are not yet available for fitting the whole dataset used in this study (see Aarva et al.\(^69,92\)), we were forced to proceed with traditional peak fitting to retain the consistency over the whole dataset. Instead, we use computational support to understand certain features that are not readily accessible from the literature, such as the peaks seen well below 285 eV in C 1s spectra of
amorphous carbon (a-C) and ta-C. An additional note on the analysis of the C 1s region is that we expect, based on the earlier studies, and the N 1s spectra recorded during this study (see Figure 1), that some of the features presently attributed to carbon—oxygen functional groups are in reality due to carbon—nitrogen bonds. However, as the amount of nitrogen present in these carbonaceous materials is very low (only the CNF and DND show any significant signal in the N 1s scans) and the analysis of the O 1s spectra corroborates much of the functional group assignment in the C 1s region (the carbon—oxygen functional group assessment), the relative contribution of intensity from nitrogen functionalities in the C 1s spectrum is expected to be small, and we cannot expect to extract any meaningful conclusions about the nature and prevalence of nitrogen functional groups from the C 1s spectra. The results from the fitting are summarized in Table 2.

The two IP positions (from HOPG and a separate ramp function to describe individual ionization of the oxygen functional groups, both of which will be discussed in more detail shortly and shown in Figure S4 in the Supporting Information) were selected to provide more rigorous and reasonable fitting results in the energy regime directly after the sp² π* and before the Rydberg states. Here, we used HOPG as a reference material whose surface has very little oxygen, as can be seen from the right column O 1s spectra in Figure 1. Importantly, the intensity increase after the π* feature on the HOPG C 1s spectra is not arising from oxygen functionalities. Instead, the observed increase is caused by the metallic-type behavior of the pure carbon matrix as described in detail in the literature and also shown in this work (no counts were collected while scanning the O 1s region). The intensity increase after the π* feature on the HOPG C 1s spectra is not arising from oxygen functionalities. Instead, the observed increase is caused by the metallic-type behavior of the pure carbon matrix as described in detail in the literature and also shown in this work (no counts were collected while scanning the O 1s region). Importantly, the intensity increase after the π* feature on the HOPG C 1s spectra is not arising from oxygen functionalities. Instead, the observed increase is caused by the metallic-type behavior of the pure carbon matrix as described in detail in the literature and also shown in this work (no counts were collected while scanning the O 1s region).

Furthermore, as discussed above, it is still likely that some of the oxygen intensities observed are arising from the silicon wafer. Especially for the graphene HT case, the relatively high intensity in the O 1s post-π region compared to the pre-σ region can be partly attributed to the featureless SiO₂ contribution. Nevertheless, in general, we note that the absolute O 1s signal is very low. Thus, both the O 1s and C 1s spectra indicate that the contribution from carbonaceous contaminants does not play a major role in the analysis, especially for the pre-σ region. The graphene CVD on the other hand, has a clear carbonyl peak at 288.63 eV and also a clear peak in the π region of the O 1s spectra, indicating higher oxygen loading than for the graphene HT.

Next, we briefly discuss the computational results and their connection to the experimental data and especially use them to interpret the low energy features observed in the C 1s spectra of a-C and ta-C. We are particularly concerned by the effect on the C 1s spectrum from added disorder and the introduction of other elements, such as oxygen. The computational spectra shown in Figure 2 highlight the drastic differences between pristine graphene, graphene with one vacancy per unit cell (see Figure 3), and graphene with oxygen-containing groups (the oxygenated structure is obtained from ref 113). The structures used in the simulations are visualized in Figure 3. The dashed lines in Figure 2 indicate the same C 1s peak attributions, with the numbering used consistently throughout this work (see Figure 1). Only relevant peak positions are depicted: (1) sp²
π*, (4) ketone, (7) C–OH, and (9) long-range order sp². Each spectrum is shifted by 0.55 eV on the energy scale to match the sp² π* peak position. Based on these quantitative results, it is clear how the features of the spectra are broadened and spectral features at low energies emerge after a defect or other elements are introduced to the pristine ordered system. As discussed in detail in our previous work,92,114 atomic-level structural models of the materials under investigation are required for constructing the XAS spectra from first principles. To have enough statistics to represent the real, nonideal materials adequately, a statistically significant sampling of computationally generated structures is required.92,114 For liquids and gases, this sampling is favorably done via molecular dynamics (MD), but this approach is not applicable for disordered solids (unless they can be treated as glasses). Since a statistically significant database of all relevant allotropes of carbon used here is outside of the scope of this study, we decided to use traditional fitting procedures for all of the structures investigated.

To further investigate the overall trends in the C 1s region, we have arranged the spectra into three distinctive groups based on the form that the carbon network takes (depending on their sp² π* intensity, peak width, and position in energy) and the presence of the long-range order. The three different distinctive groups are crystalline, mixed, and amorphous, as shown in Figure 4. All of the sp² carbon containing materials also fall into the latter category.

This classification clearly shows that any material found in this study having a long-range order in the sp² matrix will also have a clear and sharp sp² π* feature. The broader sp² π* feature seems to strongly correlate with the lack of distinctive oxygen functionalities (no clear peak in the spectra) on most of the amorphous surfaces, as none of these materials have a clear peak present in the C 1s spectra. It is possible that the decreased surface area, flatter surface features, heterogeneous surface energetics, and contributions from the dissolved oxygen in the matrix could make it unfavorable for selective functional group bonding and/or formation at the surface of the amorphous materials presented in this study. Materials in the amorphous category also include at least some degree of sp³ bonding, which is another contributing factor in the local electronic structure. Thus, instead of some groups dominating the spectra, we will observe contributions from a wide variety of different groups. The effect of the bulk, which is dominant in thin films when compared to porous networks on, e.g., SWCNTs, MWCNTs, and aligned structures of CNW and CNF, may lead to the signal from surface functional groups being overwhelmed by that arising from the bulk, as shown in our earlier work with ta-C.115

Furthermore, the materials with the clearest and most abundant presence of oxygen functional groups are those in the mixed category. Very interestingly, only carboxyl at 288.63 eV is prominent enough to show a distinctive peak for any sample. When looking at the peak intensities after the fitting procedure, as shown in Table 2, carboxyl intensity is the dominant functional group for all carbon nanomaterials, except for graphene nitride and SWCNT, which both have low oxygen content on their surface. As we have shown earlier with computational results,99,100 the carboxyl functional group is the most stable (with regard to its peak position), regardless of the environment where the COOH group is bonded (sp or sp² site), always showing a distinctive fingerprint at the same energy. At the same time, carboxyl groups, due to their chemical structure, protrude higher from the surface of the material than other functional groups discussed here, as shown quantitatively in refs 92 and 114. This makes their energy less dependent on the local chemical environment than those of the other functional groups. There have been earlier reports describing different oxygen functional groups in different environments. One excellent example, showing spectra containing sharp features around 288.6 eV, is the work of Solomon et al.25 Additionally, there seems to be a consensus that the carboxyl peak lies in the 288.5−288.8 eV region, based on much of the C 1s XAS literature. The computational results provided in refs 92 and 114 have now been able to provide the quantitative grounds for these earlier, more qualitative reports.

The sp² π* features observed, especially in Figure 4, reveal that both the position and the full width at half-maximum (FWHM) of the peak change depending on the material. For the crystalline materials, the sp² π* peak is sharp and quite well established at 285.2−285.3 eV. In addition, the excitonic feature at 291.65 eV is also clearly visible with these materials. Especially with regards to the mix of crystalline and amorphous sp² materials, namely, MWCNTs and all CNFs (which also include a higher amount of metals than the crystalline materials), there is a clear trend with the sp² π* peak appearing at lower energy and being broader than for the crystalline materials. This process is closely associated with the gradual disappearance of the sp² excitonic feature from the spectra. Broadening of the sp² π* peak is expected to arise from the differences in the electronic structure of the sp²-rich matrix when both amorphous and crystalline sp² are present. This was observed in our previous work,45,69,92 which can also explain the lower energy position of the sp² π* peak in the mainly amorphous films, as shown in Figure 2.

Interestingly, we also observe a shoulder feature in the C 1s spectra (at 284.2 eV) of the CNF, which have been grown using Ni or ta-C + Ni catalyst layers. From these, the intensity of the lower energy peak of the doublet is more prominent in the ta-C + Ni grown CNF. As has been shown in ref 58, the two types of CNFs have different structures. The Ni grown CNF has a bamboo-like structure, where the ta-C + Ni CNF has a platelet-like structure. Studies on aromatic hydrocarbons have shown a correlation between the number of isolated double bonds and a lowering of the lowest unoccupied molecular orbital (LUMO), as observed in XAS spectra16,17 and even shown to induce separate split peaks in kinetically more unstable polycyclic compounds such as tetracene and pentacene25 (on the opposite side of graphene). The lowering of the π* intensity therefore indicates the presence of more kinetically unstable sp² configurations. Theoretical calculations also indicate that the lower the energy of the peak in the C 1s spectra, the more reactive the site is expected to be.69 This indicates that the platelet-like structure would have more reactive sites than the bamboo-like fibers. Another possible explanation is discussed by Schultz et al.,116 who reported splitting of the sp² π* feature with graphene grown on different metals (Ni, Cu, Co). Graphene can produce two clearly distinct peaks in the sp² π* region when grown on polycrystalline Ni and has the ability to exhibit varying peak splitting depending on the detailed growth parameters. This is expected to arise from interactions between the metal and graphene lattice. This explanation is supported by findings from Huttmann et al.,13 where graphene was intercalated with a monolayer of Eu. While still on the Ni film, only one peak was observed, indicating that the electronic structure of
Graphene is clearly affected by the metals it is exposed to. Thus, our observation of the shoulder feature in the two different CNF systems could be explained along these lines. In both CNF grown using Ni, the resulting CNF has graphene-like sheets (either as a bamboo-like structure where the individual bamboo units are formed of graphene-like sheets in Ni grown CNF or stacked graphene sheets like in the ta-C + Ni grown CNF) and the energy difference of the sp\(^2\) \(\pi^*\) shoulder features could be arising from the differences between the Ni–C interface and interactions in the two distinct structures. Furthermore, since both Ni layers were deposited using different methods (in the Ni grown CNF sputtered and in ta-C + Ni grown CNF using a filtered cathodic vacuum arc (FCVA)), the microstructure of Ni is likely slightly different in the two cases. Finally, it is also possible that some of these observed intensities arise from highly reactive sp-sites at the interface and interactions in the two distinct structures. Therefore, since both Ni layers were deposited using different methods (in the Ni grown CNF sputtered and in ta-C + Ni grown CNF using a filtered cathodic vacuum arc (FCVA)), the microstructure of Ni is likely slightly different in the two cases. Finally, it is also possible that some of these observed intensities arise from highly reactive sp-sites at the interface and interactions in the two distinct structures. Hence, since both Ni layers were deposited using different methods (in the Ni grown CNF sputtered and in ta-C + Ni grown CNF using a filtered cathodic vacuum arc (FCVA)), the microstructure of Ni is likely slightly different in the two cases. Finally, it is also possible that some of these observed intensities arise from highly reactive sp-sites at the interface and interactions in the two distinct structures.

Based on the literature, nitrogen functionalities in a carbon matrix are often observed in graphitic, pyridinic, pyrrolic, and nitrilic forms.\(^{35,72,88,106,120}\) In contrast to photoelectron spectroscopy, N 1s XAS has been shown to provide relatively well defined and energetically separated peaks that represent the main nitrogen functionalities. We have aligned our dataset such that the second-order resonance of Ni 2p L3 (which is available as a reference in our scans) is fixed at 852.7 eV (426.35 eV in second order). For the comparison with other datasets, we applied further slight energy shifts to our dataset (+0.44 eV) to match Schiros et al. peak attribution energies. Furthermore, the following shifts were applied to other reference datasets to align them with ours (after ours had been aligned with Schiros et al.): Shimoyama et al.\(^{122}\) (+0.22 eV) and Hellgren et al.\(^{121}\) (+0.17 eV) (see Figure S4 for a detailed comparison of reference spectra to our work). Our findings also match well with the studies by Zhang et al., Che et al., Zhu et al. and Dennis et al.\(^{35,88,106,120}\)

We have indicated the most likely assignment of the main features in the dataset in Figure 1 as follows (represented by helplines): pyridinic features at 398.4 ± 0.4 eV, nitrilic features at 399.7 ± 0.4 eV, and graphitic features at 401.1 ± 0.4 eV. In the sigma region (above ∼406 eV), we observe a sharp peak in graphene\(_{\text{SVD}}\) associated with \(\sigma\) for matrixed N in graphitic-type bonding.\(^{72}\) At higher energies, we observe \(\sigma\) resonance associated with shorter C–N bonds that grow in strength as more pyridinic and nitrilic features are present (see, e.g., bond-length with a ruler, Stohr).

To further investigate the chemistry and structure of the immediate surface of the carbon nanomaterials and to compare these results with the signals originating deeper from the carbon matrix, we show the Auger electron yield (AEY, ∼2 nm probing depth\(^ {122}\)) spectra overlayed with the TEY (∼7 nm depth) spectra in Figure 5. As can be seen from Figure 5, spectral features (as in peak positions and relative intensities of peaks compared to the sp\(^2\) \(\pi^*\) peaks intensity) of all carbon nanomaterials, except for the CNF, have strong similarities to the TEY signal. However, significant differences are observed in all of the CNF samples. The AEY spectra of all of the CNF samples can be associated with a poorly defined mixture of carbon functionalities dominated by carboxyl-like groups. All spectra also display a reduction in \(\pi^*\) associated with sp\(^2\) type carbon. The absolute intensity of the AEY spectra of CNF also shows lower intensity compared to other samples (see Figure S6 in the Supporting Information). This reduced amount of carbon in the surface region is likely originating from the excessive amount of metal (nanoparticles located at the tips of the fibers (see refs 58, 82, and 124 and Figure S7 in the Supporting Information)) in comparison to other analyzed carbon nanomaterials. This would also explain the higher overall amount of oxygen observed in CNFs in comparison to other carbonaceous nanomaterials investigated here since the metallic nanoparticles at the tips of the fibers have been found to be partly oxidized.\(^{58,82,124}\)

The \(\pi\) transition region of the O 1s spectra is shown magnified in Figure 6. The results of the O 1s spectra mainly support the trends observed in the C 1s region, where carboxyl-like functional groups are most abundant in the different CNM. However, there are some cases where the global C 1s fit does not seem to completely agree with the O 1s fit, for example, in the case of the clearly visible intensity of H\(_2\)C=O/aldehyde in CNW. Based on the O 1s spectra, the only materials with significant amounts of functional groups other than the higher energy ones (carboxyl and C–OH) are SWCNT, MWCNT, all CNF, a-C, and ta-C. Additionally, for the MWCNT, it is not clear, based on the O 1s spectra, whether the increase in the H\(_2\)C=O/aldehyde intensity is caused by oxygen or can rather be induced by the broadening of the sp\(^2\) \(\pi^*\) feature.

The amount of oxygen loading on the surface of the carbon nanomaterials varies greatly. Although XAS cannot be used for quantitative analysis of the oxygen concentration, it is evidently based on the intensity of the spectra that there are differences in the amount of oxygen at the surface regions. Based on these,
the spectra can be categorized into surfaces with (i) low concentration (graphene\text{HT}, CNW, SWCNT, MWCNT, CNF(Ni), a-C, ta-C, and ND); (ii) medium concentration (graphene\text{CVD}, CNF\text{(ta-C + Ni)}, and GO); and then (iii) high concentration (CNF\text{(ta-C + Fe)}). It should be mentioned here that the O 1s spectra work as an excellent verification source for any findings in the C 1s region. The features that are truly from oxygen in the C 1s spectra must also be present in the O 1s spectra; otherwise, it would be an indication that they are not originating from oxygen but from something else. Additionally, it is of importance to note that due the complex nature of reactions taking place at the carbon nanomaterial surface, it is recommended to study the oxygen and nitrogen edges concurrently with the carbon edge to try to understand the surface chemistry of carbon nanomaterials. Although this appears to be a trivial statement, it is not always followed in practice. This can be attributed at least partly to that in X-ray photoelectron spectroscopy (XPS), and there are significant differences in chemical shift between the different edges, i.e., C 1s carries much more information in terms of the chemical shift between the functional groups than O 1s and N 1s. This makes it difficult to make direct connections between the observations in C 1s and O 1s/N 1s spectra. In XAS, there is more detailed chemical information available and due to the more detailed information available from O 1s and N 1s regions, the observations from C 1s spectra should be supported by the O 1s and N 1s data like that performed in this work and others.

All of the carbon nanomaterials in this study have very low amounts of nitrogen on their surfaces, as the absolute intensities of the N 1s spectra from all of the samples have very low counts. The only clear peak-like features are observed (from the highest to lowest counts) for ta-C + Fe CNF, ta-C + Ni CNF, DND, and Ni CNF. These materials have the highest amount of nitrogen in our dataset. The absolute intensity reveals a flat line for the rest of the materials. We can extract some more information with normalized intensity since the normalized signal reveals clear peak-shapes for SWCNT, graphene, GO, a-C, and ta-C (not in any particular order), which have medium amounts of nitrogen present. The rest of the materials, namely, MWCNT, CNW, and graphene\text{HT}, have spectra nearly identical to HOPG, which is expected to be nitrogen free as discussed earlier; we expect HOPG to be a prototypical representation of pure sp$^2$ carbon. Thus, the last group is expected to have an insignificant amount of nitrogen present. Interestingly, the N 1s spectra show clear differences in the types of carbon–nitrogen bonds present in the materials. The origin of these features is discussed in some detail in the literature. However, due to a large amount of different materials in our study and lack of computational resources to build models for solid carbon–nitrogen surfaces, it is not feasible to draw strong conclusions of what exact carbon–
nitrogen groups are on the material surface. The main trends observed in the present work are summarized in Table 3.

**CONCLUSIONS**

In this work, we have investigated several structurally diverse carbon nanomaterials and shown clear trends in their C 1s, O 1s, and N 1s XAS spectra as a function of their structural and chemical properties. Based on the observed trends, (i) there is a clear correlation between the position and shape of the sp² π* feature in the spectra, the presence of excitonic feature at 291.7 eV, and the crystallinity of the material, (ii) that carbon nanomaterials have widely different oxygen and nitrogen surface loadings, (iii) surfaces with higher oxygen concentration are the ones with no clear long-range order, (iv) nitrogen loading on the surface is more diverse than that of oxygen, and the materials dominant nitrogen group varies greatly, and (v) the amount of nitrogen on the material surface is lower than that of oxygen. Additionally, (vi) only the presence of carboxyl groups in the C 1s spectra is clearly identified as a peak, whereas the presence of other groups has to be extracted through data fitting. Importantly, (vii) the presence of carbon–oxygen bonds in C 1s spectra was further confirmed by inspection of the O 1s spectra, which should be a general practice for the verification of the results. We also exemplify how computational studies can help to understand various previously unexplained features of the spectra, such as low energy features in C 1s spectra of a-C and ta-C materials. Finally, this work also provides a systematic method of energy calibrating different C 1s spectra to compare them using an sp² long-range order at 291.65 eV as a calibration point. If the sp² long-range order is not available, then the carboxyl functional group can be used. Thus, this study serves as a reference for the chemical state and trends of carbon nanomaterials, providing an overview of the features of crystalline, mixed, and amorphous phases via XAS. Especially, our results will provide guidelines for the practitioners working with nonideal carbon nanomaterials in various fields, providing them with the previously missing map of the properties for a wide variety of nanocarbon materials. This will, for example, greatly enhance our ability to explore the connections between the electro-chemical performance and surface chemistry as well as provide us with a solid basis to create realistic computational models that can further be used to deconvolute and rationalize the experimental data.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c08597.

Cross-correlation of results with XPS; reference spectra for diamond; Raman studies of graphene CVD; N 1s XAS spectra collection from literature; C 1s absolute intensity of ta-C + Ni CNF; i0 spectra from SSRL beamline 8-2; and peak fitting examples from this work (PDF)

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Correlation between sp3-to-sp2 Ratio and Surface Oxygen Function-


Franssila, S.; Jokinen, V.; Laurila, T. SU-8 Based Pyrolytic Carbon for

Oxygen Sheets and Polycations.


