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Full Paper

Characterizing Graphitic Carbon with X-ray Photoelectron Spectroscopy: A Step-by-Step Approach

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Part of a Special Issue on Carbon in the Catalysis Community. A link to the Table of Contents will appear here once the Special Issue is assembled.

Putting carbon defects in line: High-resolution XPS and XPS depth profiling are used to characterize binding energies and spectral line shapes of sp^2 carbon, surface-defect states, and disordered carbon in highly ordered carbon nanostructures. The distinct features of these components, for example, the strong asymmetric shape of the sp^2 carbon peak changing with surface curvature and defect density, cannot be neglected in spectral analysis and require careful evaluation for a high quality deconvolution. HOPG=Highly ordered pyrolytic graphite.

Characterizing graphitic carbon with XPS @HZBde @maxplanckpress @IowaStateU

#catalyst

carbon

graphene

graphite

nanotubes

photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a widely used technique for characterizing the chemical and electronic properties of highly ordered carbon nanostructures, such as carbon nanotubes and graphene. However, the analysis of XPS data—in particular the C1s region—can be complex, impeding a straightforward evaluation of the data. In this work, an overview of extrinsic and intrinsic effects that influence the C1s XPS spectra—for example, photon broadening or carbon–catalyst interaction—of various graphitic samples is presented.

Controlled manipulation of such samples is performed by annealing, sputtering, and oxygen functionalization to identify different C–C bonding states and assess the impact of the manipulations on spectral line shapes and their binding energy positions. With high-resolution XPS and XPS depth profiling, the spectral components arising from disordered carbon and surface-defect states can be distinguished from aromatic sp^2 carbon. These findings illustrate that both spectral line shapes and binding energy components must be considered in the analysis of potentially defective surfaces of carbon materials. The sp^2 peak, characteristic of aromatic carbon, features a strong asymmetry that changes with the curvature of the sample surface and, thus, cannot be neglected in spectral analysis. The applied deconvolution strategy may provide a simple guideline to obtaining high-quality fits to experimental data on the basis of a careful evaluation of experimental conditions, sample properties, and the limits of the fit procedure.

Introduction

Carbon materials in their various forms are highly relevant to modern catalysis. Functionalization of carbon determines its catalytic performance, namely the reactivity and selectivity.^[1-5] From a chemical point of view, the different species of functional groups are well defined.^[6-10] However, to understand the underlying detailed mechanisms responsible for catalytic performance, analysis by methods that distinguish surface from depth information is often required.^[11-14] As such, X-ray photoelectron spectroscopy (XPS) is a versatile tool that can provide information on the chemical and electronic states in a catalyst surface and, within certain limits, on the near-surface region even under reaction conditions.^[15-18]

Prior to a detailed characterization, chemical and/or thermal treatments can be employed to obtain "pristine" samples.^[19-21] However, most "as-received" carbon samples appear quite heterogeneous, not only with respect to chemical bonds, for example, between carbon and oxygen, but also between the carbon atoms themselves in the form of defects, sp^3 carbon and other, disordered carbon contributions. Functionalization by forming carbon-oxygen moieties (C—O bonds), as well as any kind of defective carbon, can lead to a high number of chemical bonding environments for the carbon atoms and thus, additional peaks in the X-ray photoelectron spectrum. Although these peaks are generally minority species, they often overlap with the main component of the analyzed spectra, giving rise to alterations in the overall peak shape. Hence, a deconvolution of XPS spectra, in particular the C1s lines, into distinct species is not straightforward.

The problem of obtaining the correct peak shape for the C1s spectrum of nanostructured carbon has been faced repeatedly over the years. Often, the contributions from defects and functional groups to the C1s shape are not sufficiently considered. Furthermore, a limitation of data analysis to either the C1s region or the spectral region of the respective bonding partner only may restrict the information on which conclusions are drawn.^[22-25] Only in comparatively few publications is an interpretation of both attempted.^[26,27]

Another problem in the analysis of XPS data of graphitic carbon samples may be caused by the method itself. A graphitic carbon line shape may not only be influenced by overlapping with other carbon species but also by effects related to the electronic structure of

the specific sample, either due to the material [e.g., conducting or semi-conducting carbon nanotubes (CNTs)] or final-state effects due to the created photoelectron.^[28-30] The latter is particularly important because asymmetric peaks originating from final-state effects are not always used.^[22,31-33] Furthermore, defects and contributions of disordered carbon may add to a C1s spectrum of a graphite or graphene-based sample. Both have been discussed previously in the literature but a general agreement on how to achieve the best possible result has not yet been reached.^[34-38]

The aim of this paper as the first part of further contributions is to identify carbon species in graphite-based samples and distinguish them from their oxygen functionalities. The influence of defect-related peaks on the overall C1s line shape will be evaluated to provide suitable guidelines for the fitting procedures of the C1s region. To achieve this, various functionalized and unfunctionalized samples based on graphitic carbon have been examined systematically under various conditions, such as structural variations induced by sputtering and subsequent healing by annealing and exposure to oxidative gases (oxygen and steam). The samples surveyed include highly ordered pyrolytic graphite (HOPG), graphene [as monolayer graphene (MLG), few-layer graphene (FLG), and graphene flakes (GF)], multi-walled carbon nanotubes (MWCNTs) and single-wall carbon nanotubes (SWCNTs), graphite oxide (GO), and amorphous carbon.

Results and Discussion

Line shapes of graphitic carbon

The evaluation of different carbon and carbon-oxygen species in graphitic carbon, for example, HOPG or MWCNTs, based on XPS remains a highly debated topic. Both symmetric and asymmetric line shapes for the same carbon species have been utilized previously.^[22,31-33] Furthermore, the number of peaks used to fit more complex spectra, such as those involving numerous chemical states, can vary considerably, for both the O1s and C1s regions.^[24,25,33,39,40] Clearly, the determination of the number of species and their fitting parameters is far from unambiguous. There are several extrinsic and intrinsic effects that complicate a straightforward deconvolution of the C1s spectrum of graphitic carbon. First of all, the choice

of the photon source affects the observed line shapes. The C1s spectra of the same Nanocyl MWCNT sample as obtained by using a conventional, non-monochromatized lab source and the ISIS beamline at the BESSY synchrotron radiation facility are shown in Figure 1A. A typical binding energy (BE) window has been chosen to display the clearest changes. As expected, the C1s spectrum from the non-monochromatized lab source is notably broader than that from the synchrotron with monochromatized light. Notably, even under the latter conditions, a broadening of the X-ray photoelectron spectra is observed that is dependent on the excitation energy, due to the optical components of the beamline (see Figure S1 for the experimental resolution).

The C1s spectra displayed in Figure 1A demonstrate the possible variance in interpretations of experimental data of one and the same sample: The shape of the main intensity in the lab-source spectrum is less defined, which could directly affect the quantitative evaluation of different chemical species present in the CNT sample. For instance, the broader lab-source C1s peak could be fitted with a broader main peak or a larger number of peaks on the high-BE side of the main intensity. If the resolution is unknown, the former fitting routine could simulate a greater amount of the graphitic carbon with respect to all other species, whereas the latter may point to a larger number or higher intensity of oxygen-related components, all of which could potentially lead to misinterpretation of the measured spectrum if no further information is considered.

In many publications, either O1s or C1s spectra are discussed as a basis for chemical and, to an extent quantitative, analyses.^[22-24,41] Clearly, a combined analysis of the O1s and C1s spectra would be more accurate. However, this may be an even more complex endeavor, as is clear from the corresponding O1s spectra in Figure 1A (inset), which appear to be virtually the same, independent of the light source. Considering the distinct differences between the C1s line shapes if measured by using a lab source versus a synchrotron source, it is surprising that differences are not observed on measuring the O1s spectrum with these two sources. According to the ISIS beamline characteristics, under the experimental conditions used here, the O1s peaks are expected to be approximately 200 meV broader than a well-resolved C1s peak [i.e., C1s full width at half maximum (FWHM) \approx 0.35 eV].^[42] Hence, the

broad and somewhat blurred O1s features (spectral range 5–6 eV) and their striking resemblance to the lab-source results suggest that the O1s breadth is not limited by the bandwidth of the excitation source, rather by the presence of multiple overlapping peaks. This observation is especially notable because the O1s is often fitted with only 2 or 3 peaks, resulting in an average FWHM of at least 1.7–2 eV per peak.^[43--46] Based on the linewidth expected for the ISIS beamline, fitting with 5 to 6 peaks is feasible even if considering other broadening contributions such as heating of the sample or a higher background pressure.

A further potential source of fitting errors is the carbon itself. Naively put, highly ordered carbon should not vary much because it is always the same material. However, the spectroscopic fingerprints of different graphitic carbon forms can be quite diverse. An overview of several air-exposed multi- and mono-layered graphene-based systems is given in Figure 1B. Not only are different BE values observed but the line shapes and broadening can differ, even for nominally very similar samples, for example, HOPG and FLG. These differences may be caused partly by contaminants, disordered carbon contributions (in particular for GF on copper).^[47] and partial functionalization (oxidation) of the carbon. For graphitic carbon with its low density of states (DOS) near the Fermi energy, bonding to adsorbates or small geometric changes will change the valence band top and, hence, the position of the C1s peak. The same mechanism further affects the peak shape as it is related to coupling and relaxation phenomena caused by the C1s core hole. However, such effects are not the only sources of fitting errors. For instance, the conducting or semiconducting qualities of CNTs are known to influence the BE position with respect to the Fermi level because of the lack or presence of a small band gap.^[28]

Another striking example is provided in Figure 1C. Here, three HOPG samples were examined by using XPS directly after cleaving. The narrowest spectrum (HOPG 1) was obtained from the same sample as the broader HOPG 3. The latter actually resembled the sample HOPG 2 (also freshly cleaved), which was a different sample all together. Another sample, HOPG 4, which did not cleave well, exhibited a different BE position of the main peak to samples HOPG 2 and 3, despite showing a similar broadening. As it turned out, HOPG 4 contained Si contaminations, which may have caused a cross-linking of the HOPG

layers. Furthermore, all spectra featured slightly different $\pi \rightarrow \pi^*$ satellites, most prominently visible by an additional satellite contribution of HOPG 2 (Figure 1C, gray arrow in inset). The differences observed here suggest that layer-to-layer interactions and/or topographic effects have to be taken into account when examining graphitic samples.

The importance of substrate interactions is emphasized in the results of Figure 1D. The spectrum of as-grown air-exposed MLG on copper, heated to 500°C reflects quasi-free-standing graphene because of intercalating oxygen between copper and MLG, which eliminates the strong MLG–copper interaction.^[47] Further heating to 700°C largely removes the intercalating oxygen and restores the MLG–copper interaction, as evidenced by the shift of the main C1s peak to a higher BE. For the spectrum shown here, the deintercalation is not complete, leading to a broad shoulder on the low BE side of the spectrum. An example for strongly interacting graphene is provided by MLG on silica. Here, the line shape is quite similar to quasi-free-standing MLG but the BE clearly resembles that of the strongly interacting MLG on copper. Again, the $\pi \rightarrow \pi^*$ satellites are different, reflecting the shifts of the main intensity (Figure 1D, arrows in inset).

Fitting C—C bonds

All examples given above demonstrate that a careful deconvolution of the binding states of graphitic carbon requires a consideration and evaluation of extrinsic effects such as line broadening by excitation energy as well as intrinsic effects resulting from contaminants, the degree of functionalization and oxidation, contributions of carbon species that are different from graphite, and layer-to-layer interactions in inhomogeneous systems.

Experimental peak parameters of C—C bonds

To converge on a suitable set of fitting parameters of graphitic carbon, the role of carbon–carbon bonds will first be examined. As such, two different carbon bonding states stand out, namely sp^2 and disordered carbon. Whereas the former is well documented and usually most prominent in graphitic carbon spectra (see Figure 1C, HOPG 1), the contribution of the latter is not so well defined and, controversially, has been discussed in its potential role as defective carbon.^[34--38] A clear assessment of the electronic properties of disordered carbon

is indeed difficult. On the one hand, its spectral fingerprint is expected to be separated from that of sp^2 carbon because a long-range order should, by definition, not exist. Instead, the number of dangling bonds should increase and contribute to the electronic structure. On the other hand, a pure sp^3 -like configuration, as in diamond or CH_4 , is also not expected. Hence, disordered carbon may be considered as an intermediate between the sp^2 and sp^3 states. To achieve a sufficient amount of disordered carbon, two different approaches were used. Firstly, amorphous carbon was examined directly by using XPS and secondly, GO was heated rapidly to 250 and 1000°C. Exfoliation of GO by heating causes a transformation of various C—O—bonds firstly into other, thermally more stable, functional groups and finally a fast depletion of oxygen that exits the sample as carbon dioxide and leaves graphene-like flakes behind.^[48] Hence, on heating to 250°C most of the GO is expected to remain largely intact, whereas heating to 1000°C should increase the amount of disordered carbon due to the loss of oxygen. The C1s spectra after heating, normalized to the remaining $\pi \rightarrow \pi^*$ satellites at approximately 291 eV, are shown in Figure 2A. The fact that satellites are visible indicate that sp^2 carbon is still present in both samples, which also accounts for the maximum-intensity BE peak value of approximately 284.35 eV. The difference spectrum of both C1s spectra displayed in Figure 2B provides a fingerprint for the position, shape, and broadening of the expected disordered carbon, as it exhibits a broad symmetric peak at approximately 284.8 eV with some high-BE shoulders. Combined with the finding that the exfoliated graphite is still largely graphitic, this spectral fingerprint must originate from dangling bonds at the brim of graphite flakes. The FWHM is quite large (≈ 1 eV). This broadening may be caused by a distribution of different orientations of the dangling bonds with respect to the carbon atoms bound in a graphitic structure. Hereafter, the designation "disordered carbon" will be used synonymously for such states. Despite the exfoliation at high temperatures, both samples contain oxygen bonds as evidenced in the corresponding O1s spectra (Figure 2A, inset). As both samples were exposed to air prior to XPS characterization, the high-BE shoulders can be assigned to various C—O bonds formed after the thermal treatment.^[26]

In contrast, the more direct approach of using amorphous carbon as a fingerprint is less accurate. The comparison of the GO difference spectrum with that of amorphous carbon (Figure 2B, —) reveals that, despite a general congruence, the latter spectrum exhibits

considerably less structure, especially in the energy range of the graphitic carbon at approximately 284.3 eV. Hence, exfoliation of GO is a more suitable approach for examining disordered carbon and the rather sharp feature in the corresponding difference spectrum provides a fingerprint for its position, shape, and broadening.

In contrast to disordered carbon, represented by the high-BE feature at approximately 284.8 eV, point defects in the graphite lattice may contribute differently to the complete C1s spectrum. This is demonstrated by the comparison of commercially available MWCNTs before and after thermal treatment (Figure 2C). Whereas the amount and states of the C-O bonds barely change, as evidenced by the respective O1s spectra (Figure 2C, inset), the line shape of the C1s peak is clearly affected. The corresponding difference spectrum displayed in Figure 2D shows that apart from a slightly different graphitic intensity, a notable deviation between both peaks on the low-BE side of the spectra exists. As this difference cannot be caused by disordered carbon, the BE of which lies on the high-BE side, as shown above, it may be related to defective carbon, as has already been proposed.^[36-38] This assumption is feasible because an originally defective MWCNT surface can be improved by further graphitization at high temperatures.^[19]

HOPG as a model system

To gain a more detailed insight into the parameters required to deconvolute graphitic carbon spectra, freshly cleaved HOPG — serving as a model system for well-ordered graphite — was sputtered with argon ions under different beam conditions (see the Experimental Section). The samples were subsequently heated to 700°C to induce possible oxygen desorption and structural changes in the samples. The influence of this treatment on the electronic states was monitored by using XPS at different photon energies to allow a depth-resolved probing of the near-surface region. Surface-sensitive C1s spectra [kinetic energy of the photo (E_{kin})=150 eV] of four samples sputtered with different acceleration voltages and ion currents before and after heating to 700°C in comparison to freshly cleaved, oxygen-free HOPG are shown in Figures 3A and B, respectively. The obtained spectra were deconvoluted by using fit parameters that reflected the line shapes of disordered and defective carbon (Figure 2) and freshly cleaved, oxygen-free HOPG to ensure the best possible fits.

The fit of the freshly cleaved reference sample can be fitted with a single asymmetric component at approximately 284.32 eV ($\alpha \approx 0.095$) accounting for graphitic carbon, whereas the spectra of sputtered HOPG require mainly two more broad peaks of roughly the same intensity at 284.8 and 284.0 eV fitted without asymmetry to account for the expected disordered and defective carbon (Figure 3 A, bottom to top). For a mildly sputtered sample at low ion doses and low acceleration voltages the damage to the sample surface is small, reflected by the low intensities of disordered carbon and defects, and only slightly changes the profile of the reference peak. Applying a higher acceleration voltage with the same ion dose gives rise not only to a broadening on the high-BE side of the graphitic peak but also to a shoulder on the low-BE side that can be clearly recognized as a separate peak, which stresses the importance of introducing a defect component in C1s spectra. Furthermore, small contributions in the C—O bond region beyond 285 eV have to be added for the best fit accounting for saturated bonds by sputtering in a low-pressure oxygen atmosphere (see Figure S3).

An increase in the sputter time at low ion doses and low acceleration voltages yields approximately the same result. Only a strong increase in ion dose and acceleration voltage leads to a considerable broadening of the C1s spectrum, which has to be fitted with large disordered and defect peaks. However, by incorporating these peaks, the graphitic peak is largely diminished. Notably, the low intensity of the graphitic peak is accompanied by the lack of its asymmetric tail contributing to the background signal at higher BE values. Consequently, this leads to the introduction of more peaks in the C—O bond region on the high-BE side of the main peak.

Subsequent heating to 700°C restores the "ideal" graphitic peak shape for the samples sputtered at low ion doses and/or low acceleration voltages (0.5 or 1 kV, 0.1 μ A, 3 min), whereas the spectrum of the sample sputtered under mild conditions for a longer time (0.5 kV, 0.1 μ A, 24 min) follows the trend but cannot be restored to the solely graphitic peak shape (Figure 3B). This trend is confirmed by corresponding scanning tunneling microscopy (STM) images taken after heating to 700°C, which show barely any defects for the samples sputtered at 0.5 or 1 kV and 0.1 μ A for 3 min, whereas the long-time sputtered sample exhibits a high

density of point-like defects (Figure S2). The heavily sputtered sample also shows some changes in the X-ray photoelectron spectra indicating a partial restoration but the effects are small compared to the other samples. For this sample, no STM image resolving the atomic surface could be produced.

The results depicted in Figure 3A and B confirm the usefulness of the fitting strategy based on the observations from different graphitic carbon samples examined above. However, the loss of the graphitic component for a heavily sputtered sample surface makes clear that the fit strategy may have its limits. To explore these limits further, XPS depth profiling was performed (Figure 3C).

In general, samples sputtered with a low acceleration voltage and low ion dose are expected to show (point-)defect-like surfaces. Ions can penetrate the first or even deeper layers but the mixing effect caused by argon ions should be rather small because of the small ion dose.^[49-51] Increasing the acceleration voltage would lead to a largely intact surface, but a more heavily affected subsurface, due to the higher kinetic energy transferred from the decelerated ions to the lattice.^[50] An additional increase of the ion dose would also damage the surface layer due to the higher number of impinging ions. These effects can be observed with depth profiling by comparing the surface-sensitive with the depth-sensitive C1s spectra in Figures 3A and C, respectively. Although the surface-sensitive spectrum of the mildly sputtered sample (0.5 kV and 0.1 μ A for 3min) exhibits only marginal contributions from disordered carbon and defects, these peaks are more intense in its depth-sensitive counterpart, in particular the defect component. Increasing the acceleration voltage leads to even higher intensities of both components in the depth-sensitive spectrum with a slight increase in intensity of the disordered carbon peak with respect to the defect peak. This trend continues for the long-time sputtered sample, for which the disordered carbon peak is clearly stronger than the defect peak. This finding is expected because the larger mixing effect would cause more damage to the HOPG lattice. Finally, the spectra of the heavily sputtered sample (1 kV and 1.5 μ A for 3 min) do not differ much across the two probing depths, which supports the interpretation that the spectra represent a heavily damaged surface. However, the deconvolution of these spectra clearly represents the limit of a meaningful assignment of

defects because the corresponding peak is more intense than the graphitic peak, which should represent the original material.

In this section, it was illustrated by deliberately creating defects and disordered carbon reference surfaces by sputtering and subsequent heating of HOPG that the concept of fit parameters derived from the comparison of differently thermally treated GO samples and the assignment of the low-BE shoulder of graphitic carbon to defects is feasible. In particular, the results obtained by XPS depth profiling reveal that the fit strategy is not only applicable, it also stresses that there are certain limits involving the definition of defects in graphitic carbon. The presence of defective, disordered, and sp^2 carbon species seems to be independent of the nature of the sample, for example, HOPG or MWCNT, if the basic material is graphitic. However, there are small differences in the line broadening of disordered and defect peaks between sputtered HOPG and MWCNTs, which indicates that both peaks may represent a number of different states, for example, different defect sites or a distribution of dangling bonds in different orientations (see Table 1).

Further influences on C1s peak shape

Aside from the ratio between sp^2 , disordered, and defective carbon, the fit procedure presented above may have additional repercussions that need to be evaluated. In particular, the quantification of C—O bonds on the basis of O1s and C1s spectra may be affected by the line shapes of peaks representing C—C bonds. Contributions of C—O bonds are almost completely confined to the BE region between the C—C bonds on one side of the C1s spectrum and the $\pi \rightarrow \pi^*$ satellite on the other. Hence, the tails and shoulders of these peaks, notably the asymmetric tail of the sp^2 peak, can form a quasi-background signal for the C—O bond-related peaks. A simple test can be performed by comparing the cross-section-corrected integrated O1s intensities of a sample to the remaining C1s intensities after subtracting defect, sp^2 , and disordered carbon and satellite contributions (see the Experimental Section). Firstly, this procedure was applied to the sputtered HOPG samples, as displayed in Figure 3. As already apparent from the fits displayed, the contributions of carbon bonded to oxygen were expected to be small except for the heavily sputtered surface.

The comparison of C—O bond-related O1s and C1s intensities is displayed in Figure 4A for a mildly sputtered HOPG surface. The deviation between both appears to be small and, assuming a maximum error of 50% (see the Experimental Section), it is still within the error range. Interestingly, this trend was confirmed for all samples examined in this work consisting of largely planar graphitic carbon. For those samples an asymmetry parameter of $\alpha \approx 0.095$ could always be used for fitting sp^2 carbon (Figure S3B, left). However, for CNT samples with curved surfaces and an undefined CNT orientation within the sample, the same asymmetry parameter led to a considerable deviation of the amount of C—O bonds derived from the O1s and the C1s spectra. An example is given in Figure 4B (top panel). Here, a fresh MWCNT sample was functionalized and subsequently heated to 540°C followed by two reoxidation-reduction cycles in oxygen and water, respectively. The fraction of C—O bonds derived from the C1s spectra was always roughly 10% higher than the corresponding (and more accurate) amount derived from the O1s region. These values were clearly outside of the error bar (error \approx 50%). Only by leaving the asymmetry parameter free during the fit procedure could the C1s-related C—O bond peak intensities be lowered to the expected range (Figure 4B, bottom). This behavior was also observed for several other MW- and SWCNT samples (see Figure S3A, B). Apparently, to properly account for C—O bonds in these samples the asymmetry of the graphitic carbon peak has to be increased. This behavior points to an intrinsic effect that may be related to charge redistributions within the CNTs because of their curved surfaces. However, although still within the error for all best fits presented here, neither the planar nor the curved carbon samples yield exactly the same values for C—O bond fractions derived from the C1s and O1s spectra, respectively.

Peak identification

Defects of graphitic carbon are usually held responsible for the change in the XPS line shapes, however, it is under debate at which BE values spectral changes due to defects can be expected. Defect-like carbon has been described to manifest as a peak at approximately 285 eV,^[34,35] whereas elsewhere its position is claimed to be on the opposite side of the sp^2 related peak (\approx 284.3eV) at approximately 284.0 eV.^[36-38] For HOPG, even a surface core-level shift has been introduced to the discussion.^[52-54] However, considering the BE position relative to

the main intensity found for this surface core-level state, it is rather related to the high-BE component at approximately 285 eV. Although both assigned as defects in different publications, there must be a difference between these two species separated by a BE difference of at least 0.8 eV. As apparent from the results shown in Figure 1, several intrinsic and extrinsic effects can superimpose and make identification difficult. The problem is resolved by combining synchrotron-based depth resolution after controlled destruction and healing of a well-known reference material (HOPG) by sputtering and subsequent heating with results obtained after thermal reduction of GO and MWCNTs (Figures 2 and 3). The two different contributions to the C1s spectra can be clearly assigned to disordered carbon and defect-like graphite, respectively. In the data presented above, both features can be present simultaneously, independent of the sample material such as HOPG or MWCNTs.

Hence, it can be concluded that both features under debate are different sides of the same coin: less-perfectly ordered carbon surfaces will feature a component representing rather point-like defects and a disordered carbon peak representing dangling bonds at the brim of locally graphitic material. Both defective species may be caused by either the manufacturing process (e.g., by growing MWCNTs) or more extensive destruction of the graphite lattice.^[19,55] In that sense, both can be considered "defects", combining the results presented in previous publications.^[34-38] However, this peak assignment has its limits. One example is the degree of destruction and disorder of the graphite lattice as shown in Figure 3 (topmost panels), which results in disordered carbon and defect peak intensities exceeding that of the basic graphite material. Another example is provided by the line broadening of the disordered carbon and defect peaks (see Table 1). Although still narrower than for exfoliated GO (Figure 2B), peaks observed for sputtered HOPG are broader than for functionalized MWCNTs. For the defect contribution, a possible explanation for the broadening is an overlap of several adjacent peaks originating from different defect sites as proposed by Barinov et al.^[38] A sputtered HOPG surface may feature a broader range of defect sites than a functionalized MWCNT. A similar scenario may apply to disordered carbon, for which a superposition of different orientations of the dangling bonds with respect to the carbon atoms bound in a graphitic structure may cause the broadening. This would also explain the large broadening with exfoliated GO, which is expected to be the most "defective" sample under examination

in this work. Hence, considering that many superimposing influences potentially hamper a straightforward interpretation of C1s spectra, the data must be analyzed carefully with regard to the origin and nature of any given graphitic sample.

Line shape

Apart from the overlap of different peaks representing different species, line-asymmetry of the sp^2 carbon, described by its asymmetry factor α , is the most prominent feature of the observed line shape in the C1s spectra. Asymmetry for a non-metal, such as carbon, is unusual because of the lack of a high DOS near the Fermi energy, which would be required to cause final-state effects as in metals leading to asymmetries.^[56,29] Yet, for graphitic carbon the origin of asymmetry can be explained in a similar way on the basis of core holes left after excitation of photoelectrons.^[57] These holes have to be screened by relaxation of the remaining electrons, leading to excitation of electrons of the valence band to unoccupied states in the conduction band and causing the escaping photoelectrons to lose energy. The resulting asymmetry is expected to be independent of interlayer interactions, which explains why amorphous carbon materials, such as activated charcoal, can also feature asymmetric line shapes.^[29] The asymmetry is often neglected on fitting C1s spectra, which may potentially lead to misinterpretation of the data with respect to the number of species present in a certain sample and their quantification.^[32,33] In contrast to, for example, sp^3 carbon, which lacks any asymmetry, the asymmetry parameters commonly determined for HOPG are in the range of $\alpha=0.15$.^[29,57,58] Occasionally, lower values are reported.^[58-60] In the data presented above, for graphitic carbon values between $\alpha=0.095$ (HOPG and graphene) and 0.18 (as-received MWCNTs) were observed. Whereas the former value is rather low and to be expected only for graphene,^[47,61] the latter is higher than that expected of HOPG. This is of particular importance because HOPG is commonly used as a model and reference system for graphitic carbon in XPS. As stated above, different α values are reported not only in the literature but also clearly visible in Figure 1C, in which several different spectral shapes were observed for freshly cleaved HOPG. A feasible explanation for these differences is provided by considering perturbations affecting the delocalization of the π orbitals. In a well-ordered graphitic carbon system the 2p orbitals overlap and delocalize.^[62] The presence of defects

and/or bends in the graphite layers can disturb the delocalization.^[63] The localized charges at defects need to be screened, which results in an increased asymmetry of the graphitic carbon peak if the damage to the graphite structure is not too large, that is, the defect density is small.^[64] More severe damage will increase the defect density until the localized charges cannot be screened efficiently. This will lead finally to the appearance of defect and disordered carbon peaks, respectively. The change of the asymmetry parameter as a first indication of the presence of defects may also explain the different asymmetries observed for HOPG. Here, depending on the quality of the sample material, the cleaving procedure may lead to point defects and step edges contributing to the asymmetry.

However, considering the results displayed in Figure 4 for functionalized MWCNTs, the influence of defects on the asymmetry appears to be rather small. This is evidenced further in Figure S3 B, which shows the comparison of C—O bonds derived from C1s and O1s spectra of planar samples and unfunctionalized MWCNTs and SWCNTs. A small difference is apparent between the asymmetry of as-received and heated MWCNTs, which may account for the influence of defects in the as-received sample. Yet, the difference is only a fraction of the increased asymmetry required to derive reasonable C—O bond fractions from the C1s region in agreement with the C—O fractions based on the O1s intensities. Hence, another effect has to be considered that is more likely to be responsible for the larger asymmetry, namely, the change in the whole electronic structure due to the curvature of the CNT.

It is well known that the curvature has a large effect on conductivity, chemical reactivity, and the interaction between individual CNTs.^[65-69] The bent surface causes a rehybridization within the CNT walls that displaces the charge distribution outwards and can change the electronic states near the Fermi energy.^[70-72] Goldoni et al. observed such an effect for SWCNTs examined by local soft X-ray spectromicroscopy and proposed that a higher DOS than graphite is responsible for the increased asymmetry.^[73] Thus, the enhanced asymmetry required for deconvolution of CNT-related C1s spectra is assigned to curvature effects.

Clearly, to perform a meaningful fit of graphite-based samples the introduction of an asymmetric tail to the graphitic peak cannot be neglected. This may be of particular

importance because the asymmetry factor can provide a useful experimental tool to estimate contributions of well-ordered carbon in largely graphitic materials, for example, coal or graphene.^[29,47,61] For the latter case, this method may even provide more detailed information. Whereas quasi-free-standing graphene on copper (or transferred graphene, see Figure 1) is fitted with an asymmetry factor of $\alpha=0.095$, coupled graphene exhibits a slightly broadened line on the high-BE side. The broadening was explained previously by the presence of an additional peak, featuring contributions from the brim of growing graphene islands.^[47] In contrast, graphene on nickel, in all its differently interacting forms (e.g., as epitaxial or rotated graphene), requires a higher asymmetry of $\alpha=0.14$.^[74] Hence, the asymmetry may also include information on the strength of interaction of graphene with its substrate. A detailed investigation is currently in progress.

Other influences on the deconvolution of C1s spectra

Another important influence on line shapes in the C1s spectra includes the background subtraction. In all spectra presented in this work the BE region was usually recorded between 280 and 300 eV and even up to 360 eV for HOPG. A linear background on the low BE side was always subtracted and only a small Shirley background was required for a reasonable fit quality. However, background subtraction is frequently found to be performed rather crudely by subtracting a linear background underneath only the main peak region, neglecting even the presence of the $\pi \rightarrow \pi^*$ satellite, in addition, the chosen energy window may be small. In light of the asymmetry (which, in principle, provides a peak with an infinite tail) and its influence on quantification and quality of the fits, as discussed above, the background subtraction becomes even more important. Furthermore, the extensive satellite and energy-loss region may have to be taken into account if the samples under investigation are more complex than HOPG. Even for HOPG, satellites and the energy-loss region can change considerably, both qualitatively and quantitatively, with different excitation energies (Figure S4). As the slope of the energy-loss region is dependent on the number of inelastically scattered photoelectrons (i.e., the escape depth), the background of the satellites may be distorted leading to errors in the fits if a background is not applied carefully.

Conclusions

It has been shown that intrinsic and extrinsic effects, for example, carbon–catalyst interactions or photon broadening, can have a strong effect on C1s line shapes and their BE positions, something that is often neglected in the evaluation of X-ray photoelectron spectra. Identification of disordered carbon and surface defect components allows a high quality deconvolution of C1s spectra and demonstrates that both components have to be considered if analyzing potentially defective surfaces of graphitic carbon. The spectral feature representing the graphitic carbon itself exhibits a strong asymmetry that cannot be neglected with respect to quantification, for example, of carbon–oxygen bonds. This is of particular importance because the asymmetry has been found to vary with dependence on the surface geometry of the graphitic carbon, namely the curvature of the surface. However, the fit strategy presented in this work has its limits with respect to the degree of damage to the graphitic carbon and the accuracy with which contributions other than from carbon–carbon bonds can be determined. Hence, a careful evaluation of the experimental conditions and the sample properties prior to an X-ray photoelectron spectroscopic analysis is imminent.

Experimental Section

Sample preparation

Several different graphite-based samples were examined in this work. Details on sample material and preparation are provided in Table S1. HOPG (Mateck, ZYB grade) was freshly cleaved in air and immediately transferred to a standard laboratory ultra-high vacuum chamber [base pressure= 10^{-10} mbar (1 mbar=100 Pa)]. To degas the sample, the HOPG was heated in ultra-high vacuum up to 1000°C. Subsequently, the sample was checked for contamination by using a lab-source X-ray photoelectron spectrometer [MgK $_{\alpha}$ excitation (1253.6 eV), hemispherical analyzer Phoibos 150, both Specs GmbH]. Different sputter procedures were performed by bombarding the samples with Ar $^{+}$ ions (Ion Source IQE 12/38) at various acceleration voltages, sample currents, and times to achieve different penetration depths and ion doses, respectively. The effective sputter depths z were calculated by using Equation (1):

$$\dot{z} = \frac{j \times Y}{e \times N_A} \quad (1)$$

in which j is the current density, Y the sputter yield, e the elementary electric charge, and N_A the density.^[75] These values serve as a guideline to distinguish between different degrees of surface damage. To avoid uncontrolled functionalization during transport in air, the sputtering was performed under mildly oxidizing conditions to saturate dangling bonds with O₂ ($P_{O_2}=5.1 \times 10^{-6}$ mbar). After sputtering, the samples were transferred in air to the ISIS beamline located at the BESSY synchrotron facility for characterization by using near-ambient pressure (NAP)-XPS. During characterization all samples were heated to 700°C to allow for thermal reduction and structural improvement.

All MWCNT samples were based on commercially available Nanocyl CNTS (Nanocyl 3100). A detailed characterization can be found elsewhere.^[19] To characterize the effect of defect structures and carbon contaminations, such as amorphous carbon, on X-ray photoelectron spectra, as-received MWCNTs were heated to 2250°C. One part of the sample material was subsequently transported to the ISIS beamline in air, pressed into pellets, and characterized by using NAP-XPS at RT. Prior to XPS analysis, the remaining part was functionalized with concentrated HNO₃ for 2 h at 100°C. After functionalization, XPS surveys confirmed the presence of O and C only in the samples. During characterization these samples were heated to 540°C to allow for thermal reduction. The reduction was followed by reoxidation at RT by exposure to O₂ and H₂O at 0.1 mbar, respectively. After each reoxidation the samples were thermally reduced by heating to 700°C in vacuo.

Standard SWCNT and amorphous carbon materials were provided by TU München and UCam, respectively. SWCNTs were based on commercially available Nanolab Inc. CNTs treated in a Cl₂/He mixture. Amorphous carbon was sputter-deposited as a 2 nm-thick film on a native Si oxide on a Si wafer. Both samples were kept in air prior to XPS analysis. XPS surveys confirmed the presence of mainly O and C with some traces of Cl or P contamination.

GO powder was obtained by liquid-phase oxidation following Hummer's method. The GO powder was subsequently heated to 250 and 1000°C to allow for different degrees of reduction. The samples were transported to the ISIS beamline in air prior to XPS analysis.

GF, MLG, and FLG were grown on polycrystalline Cu foil by chemical vapor deposition of C₆H₆. Growth parameters and XPS characterization methods are described in detail in Ref. [47]. MLG grown on Cu foil was wet-chemically transferred onto SiO₂ on a Si wafer. All samples shown in this work were exposed to air prior to thermal treatment in vacuo.

XPS

NAP-XPS experiments were performed in the NAP-XPS setup at the ISSS beamline of the FHI located at the BESSY II synchrotron radiation facility in Berlin, Germany.

The setup consisted of a reaction cell attached to a set of differentially pumped electrostatic lenses and a separately pumped analyzer (Phoibos 150 Plus, Specs GmbH), as described elsewhere.^[76] The spectra were collected in normal emission in vacuo with a probe size of approximately 150×80 μm. The samples were heated from the back by an external IR laser (continuous wave mode, λ=808 nm). The temperature was controlled by using a K-type thermocouple in direct contact with the sample surface. Possible sample contamination was checked for in survey spectra at the beginning of each experiment. To obtain depth-resolved information, the photoelectron spectra were measured at various photon energies for each element. The corresponding kinetic energies of the photoelectrons and their electron mean free paths are summarized in Table S2. For the most commonly used photon energies in this work—O1s: $h\nu=680$ eV, C1s: $h\nu=425$ eV—the total XPS information depths were approximately 2 and 5 nm, respectively. That is, 95% of all detected electrons originated from a depth of 3λ below the sample surface.^[77] Owing to the different photon energies, the spectral resolution varied between approximately 0.35 and 0.5 eV (see Figure S1 for details).

To ensure an accurate XPS analysis, a three-step calibration of the BE values was performed. Firstly, C1s spectra of pure carbon samples (i.e., without substrate) taken at the same photoelectron kinetic energies as the corresponding O1s spectra (i.e., the same information depths) were compared to C1s spectra taken at the same photon energy as the O1s spectrum. Secondly, the spectra were referenced to the Fermi edge if possible (MLG, GF, and FLG all on Cu substrates). In a third and last step, pure carbon samples were cross-referenced by comparing the BE values of their C1s and O1s spectra against the C1s and O1s peak positions determined at the same photon energies from samples with a visible Fermi edge. All

spectra were normalized to the incident photon flux. The photoionization cross section was considered according to the calculations of Yeh and Lindau.^[78] Background correction was performed by using a Shirley background.^[79] The C1s spectra were fitted following the Levenberg–Marquardt algorithm to minimize the squares of the deviations (χ^2). Peak shapes were modeled by using Doniach–Sùnjić functions convoluted with Gaussian profiles so that an asymmetric line shape could be fitted when required.^[80] The accuracy of the fitted peak positions was approximately 0.05–0.1 eV. An overview of the fitted main components of the C1s region is given in Table 1.

For semi-quantitative analysis, the relative abundance (in %) of C and O for various samples was calculated from the measured integral O1s and C1s intensities weighted by their respective escape depths and photoionization cross sections. Contributions of components in the C1s region were calculated by considering the respective fractions obtained from the best fits with respect to the total intensity of each spectrum. The error was conservatively estimated to be approximately 50% of the relative abundance.

STM

STM images of HOPG after XPS characterization were produced in air on a Digital Instruments Nanoscope III microscope by using a tip cut from Pt-Ir wire.

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Figure 1.A) C1s spectra of a MWCNT sample as obtained at ISIS [BESSY; photon energies of 585 eV (C1s) and 830 eV (O1s), —] and from a conventional lab source [electron spectroscopy for chemical analysis (ESCA) MgK_α, —]. Inset: Corresponding O1s spectra. B) C1s spectra of different carbon materials at RT. C) C1s spectra of freshly cleaved HOPG. HOPG 1 and 3 are from the same block after different cleaving attempts. HOPG 2 and 4 are different samples. Inset: Corresponding $\pi \rightarrow \pi^*$ region in detail. D) C1s spectra of MLG on Cu at 500 and 700°C, respectively, and after transfer to SiO₂ and subsequent heating to 450°C to remove contaminants. Inset: Corresponding $\pi \rightarrow \pi^*$ region in detail.

Figure 2.A) C1s spectra of exfoliated GO heated to 250 and 1000°C, respectively. Inset: Corresponding O1s spectra; cps=counts per second. The samples were kept in air after thermal reduction. The intensities correspond to 3--4% residual oxygen. B) Difference spectrum of both C 1s spectra in Figure 2A (1000–250°C, —) in comparison to a spectrum of amorphous carbon (—). The latter is normalized to the highest intensity of the difference spectrum for better comparison. The small difference in the graphite contributions at 284.35 eV in the difference spectrum stems from the normalization to the $\pi \rightarrow \pi^*$ satellites. C) C1s spectra of MWCNTs as received and after heating to 2250°C. Inset: Corresponding O1s spectra. D) Difference spectrum of both spectra in Figure 2C.

Figure 3.A) C 1s spectra of freshly sputtered HOPG at $E_{kin}=150$ eV. The sputter parameters are indicated in the panels. B) The spectra of the same samples after subsequent heating to 700°C. For comparison, the C1s spectrum of freshly cleaved, oxygen-free HOPG is displayed (bottom). The effective sputter depth estimated from the sputter parameters ranges from 0.008 to 0.02, 0.06, and 0.29 nm and should be considered as a guideline to distinguish between the various sputter conditions (from bottom to top). C) Depth-resolved spectra of the freshly sputtered samples measured at $E_{kin}=700$ eV. For fit details, see Table 1.

Figure 4.A) Comparison of quantitative analysis of C1s and O1s spectra of sputtered HOPG recorded at $E_{kin}=150$ eV at different temperatures (see Figure 3). B) Comparison of quantitative analysis of C1s and O1s spectra of functionalized as-received MWCNTs during thermal reduction and reoxidation. The reoxidation, labeled "20(O₂)" and "20(H₂O)", was

performed under O₂ and H₂O atmospheres, respectively, at 0.1 mbar. Subsequent reduction was achieved by heating to 700°C.

Table 1 Overview of the fit parameters used in this work.^[a]

Sample (conditions)	T [°C]	sp ² Peak [eV]	FWHM [eV]	α	Disordered carbon peak [eV]	FWHM [eV]	Disordered carbon peak [eV]	FWHM [eV]
HOP 1, reference		284.3	0.35	0.095				
HOPG (0.5 kV, 0.1 μ A, 3 min)	RT	284.3	0.5	0.095	284.8	0.9	283.9	0.8
	700	284.3	0.4	0.095				
HOPG (1 kV, 0.1 μ A, 3 min)	RT	284.3	0.55	0.095	284.8	0.9	283.9	0.8
	700	284.3	0.45	0.095				
HOPG (0.5 kV, 0.1 μ A, 24 min)	RT	284.3	0.55	0.095	284.8	0.9	283.9	0.8
	700	284.3	0.55	0.095	284.8	0.9	283.9	0.8
HOPG (1 kV, 1.5 μ A, 3 min)	RT	284.4	0.55	0.095	284.7	1.05	284.0	0.8
	700	284.4	0.55	0.095	284.7	0.95		
MWCNT, functionalized (ar) ^[b]		284.4– 284.55	0.55– 0.65	0.19– 0.22	284.7	0.55	283.8–284.0	0.55

MWCNT, functionalized	2250	284.3– 284.45	0.55	0.13– 0.15	284.7	0.55	284.0	0.55
MWCNT, unfunctionalized (ar)		284.45	0.55	0.14	284.65	0.55	283.9	0.5
MWCNT B, ^[c] unfunctionalized (ar)		284.45	0.6	0.16	284.8	0.5	284.0	0.5
MWCNT, unfunctionalized	2250	284.35	0.45	0.14	284.65	0.55	284.0	0.5
MWCNT B, unfunctionalized	2250	284.35	0.45	0.14	284.65	0.5	284.0 ^[d]	0.55
GF	250	284.4	0.5	0.095	284.75	0.6	284.0	0.55
MLG	500	284.35	0.5	0.095			284.1	0.55
FLG	300	284.4	0.55	0.1	284.7	0.6	284.0	0.55
FLG	600	284.35	0.55	0.1	284.7	0.6	283.9	0.6
SWCNT (ar)		284.5	0.55	0.14	284.7	0.5	284.05	0.55
SWCNT	200	284.45	0.55	0.14	284.7	0.5	284.05	0.55
SWCNT	400	284.45	0.55	0.14	284.65	0.5	284.05	0.55

[a] For functionalized MWCNTs the various experimental steps are summarized, thus, only BE and FWHM ranges are given (for experimental details, see Table S1). [b] ar=as received. [c] MWCNT B=new sample from the same batch as MWCNT. [d] Very low peak intensity.