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X-ray photoelectron spectroscopy study of the interaction of lithium with graphene

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Abstract:

Graphene-like nanostructures, solely or in combination with redox active compounds, are an important component of battery electrodes. Design of effective electrode materials requires a deep understanding of electrochemical reactions occurring at graphene surfaces. The methods of X-ray photoelectron spectroscopy (XPS) are very helpful in such research, providing the composition of studied samples and electronic state of individual elements. In this chapter, we demonstrate advantages of XPS for monitoring of chemical vapor deposition graphene growth and lithium penetration under graphene layers, disclosing of interactions with metals and interface states.

Keywords: CVD graphene, graphene/metal interface, nitrogen doping, batteries, X-ray photoelectron spectroscopy, synchrotron radiation

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Starting from 1991, lithium-ion batteries have been widely used in various electronic devices [1]. Currently, graphite serves as a standard electrode material owing to its low weight, electrical conductivity and low intercalation potential relative to lithium [2]. The growing human demands require batteries with high power and high energy, which however, are not provided by graphite. This is why a vigorous search for new nanostructured carbon-based materials being able to sustain large current densities is being conducted [3]. Graphene, a monolayer of graphite, is a perspective unit for the construction of these materials and a good model system for the investigation of their interaction with lithium. Particularly, it has been shown that adsorption of lithium on both graphene sides increases the specific capacity almost twice as compared to graphite [4].

In a nanostructured material, lithium can adsorb on the surface and intercalate between graphene layers or into the graphene-metal interface space of a multicomponent system. X-ray photoelectron spectroscopy (XPS) can help to understand these processes by studying graphene layers located on different substrates including metallic ones. XPS provides spatial and depth resolution of the species bulk or interface as well as local potential energy variations along lateral directions with nanometer and sub-nanometer accuracy of the interface depth profile in an element-specific way. This allows studying the interfacial phenomena in Li-ion batteries such as electrolyte/electrode interactions [5] and formation of solid electrolyte interface film [6] and the chemical and structural changes of electrode material upon a lithium insertion/extraction [7]. The application of XPS becomes especially important, when contact with air of the studied system should be avoided between the steps of its preparation and measurement. Lithium is readily oxidized and its deposition on the graphene surface by vaporization of a lithium dispenser in a vacuum chamber of the XPS spectrometer is a proper approach to exclude unwanted contaminations.

This chapter presents a few striking examples of XPS studies of lithium interaction with single-layer and few-layer graphene, including nitrogen-doped graphene, which has been grown by the chemical vapor deposition (CVD) method. We start with a short introduction to present XPS feasibility for very thin films and control of the CVD graphene growth by fast XPS and characterization of graphene/metal interface. We then continue with an XPS study of electronic states in graphene on a metal substrate before and after lithium deposition

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and finish with revealing of influence of nitrogen inclusions on the properties of interaction of graphene with lithium.

1 XPS introduction

Since its invention by Kai Siegbahn in 1954, XPS, which is also known as electron spectroscopy for chemical analysis (ESCA), is widely used for investigating and characterizing properties of materials that include elemental composition and empirical formula [8]. XPS allows to disclose the chemical state and unravels the electronic states of the elements within the studied materials. Being a surface-sensitive technique, XPS is an essential instrument in surface science and is actively used for investigation of low-dimensional materials.

In an XPS experiment, a sample of the studied material is irradiated by an X-ray beam, and the kinetic energy (KE) of the emitted photoexcited electrons is analyzed in the recorded XPS spectra. Due to energy conservation, the entire photon energy ($h\nu$) is absorbed by a core-electron of an atom with binding energy (E_B), which escapes the sample with KE (E_{kin}) reduced by the work function Φ of the material:

$$E_{\text{kin}} = h\nu - E_B - \Phi$$

This equation allows to construct a photoelectron distribution as a function of E_B . Since each element has its own set of XPS peaks at characteristic binding energies, the recorded XPS spectra thus contain sophisticated information on the chemical composition and related properties of the studied material. As the measured quantity is the KE of the photoelectrons, the escape depth is limited by the inelastic mean free path (IMFP) of the electrons due to inelastic collisions making XPS and ESCA measurements highly surface-sensitive techniques. In that regard, XPS is exceedingly demanded for the characterization of low-dimensional materials and in particular has been intensively and widely used in studies of graphene and graphite-based compounds.

Photoemission (PE) experiments can be performed in the laboratory where as source of light a gas-discharge lamp in combination with an X-ray tube is used allowing to obtain PE spectra of the valence band and core levels of the sample. Nevertheless, a synchrotron radiation facility offers much broader opportunities for the experiments. The synchrotron source covers an essentially larger photon energy range, and in difference to laboratory-based sources it allows to precisely select the desired photon energy using a monochromator, which picks the energy from a continuous spectrum over a wide energy range. Another essential advantage of a synchrotron radiation facility is the very high intensity, brightness, variable polarization and small size of the photon beam. A limiting factor can be the restricted time for each scheduled experiment since the available beam time is distributed among many user groups.

Figure 1 shows a photograph and a schematic presentation of the experimental station of the Russian-German beamline of the BESSY-II facility. The station was designed in a way to be highly flexible and to achieve a reliable performance for the broad variety of experiments. It consists of three chambers. The PE measurements are performed in the analytical chamber, which is equipped with an electron-energy analyzer, a low-electron-energy diffraction system, a partial yield electron detector and an X-ray tube. Optionally, a few flanges can be used to mount evaporator sources. This allows time-dependent experiments where metal deposition and PE data acquisition are done simultaneously. It is important to note that only rather non-reactive materials like Ag, Au, etc. can be used for this purpose. The chamber positioned right above the analytical chamber is dedicated for “clean” experiments with rather delicate and reactive materials like rare-earth compounds. It is equipped with a quartz microbalance, flanges to mount evaporators, a gas-inlet system, a flash machine, a wobble sticks, an ion gun, several windows, a manipulator and a fast-entry system. Here, thin films can be deposited in-situ using Knudsen-cell-type evaporators. Surfaces of bulk samples can be prepared by several methods: cleaving, sputtering, scraping and heating up to 2,000°C. The “side” preparation chamber is used for investigations of “fragile” organic and biological molecules which generally show enhanced sensitivity to X-ray damage effects. This chamber has a similar set of insertion devices as the “top” one, but is better suited for such delicate materials as organic molecules, polymers, proteins or DNA.

Figure 1: (a) Photograph of the experimental station at the Russian-German beamline at BESSY-II. (b) Schematic 3D model of this station. It consists of (1) electron-energy analyzer, (2) analytical chamber, (3) “top” preparation chamber, (4) “side” preparation chamber, (5) and (6) sample manipulators, (7) and (8) fast-entry system, (9) magnetically coupled sample transporters.

There, essential attention was given to the analysis of the C 1s XPS spectrum, which contains information on peculiarities of the carbon-based matrices. Moreover, XPS can be applied in time-dependent mode combining the data acquisition process with the studied physical process or chemical reaction allowing to comprehensively explore their kinetics. As an example, below we show an application of this approach for the exploration of growth and properties of graphene on a nickel surface [9–11].

2 Fast or time-dependent XPS

Figure 2(a) presents a time-dependent data set taken in the vicinity of the C 1s emission line during the CVD synthesis of graphene on a fresh Ni(111) film epitaxially grown on a W(110) substrate [10]. Every 10 s, one XPS C 1s spectrum has been taken. Inspecting the spectra, it becomes evident that the prepared Ni(111) film contains a certain amount of carbonaceous contaminations that are reflected by feature A at 283 eV binding energy (BE). Fortunately, these contaminations do not interfere with the graphene growth, as they are fully removed during the first 200 s while the sample heats up. When the sample temperature stabilizes at 511°C, any signatures of carbon contaminations vanish, thus the nickel surface is perfectly clean. Afterwards, propene C_3H_6 gas is gradually introduced into the experimental chamber, until after about 500 s a partial pressure of 2×10^{-7} mbar is reached. Immediately after starting the propene gas supply, the spectral pattern of C 1s reveals a distinct manifold feature at 283 eV BE. After another 100 s, a new feature B at 284.7 eV becomes visible with rapidly increasing intensity. This peak is a signature of the formed graphene on the nickel surface. The saturation of feature B indicates the completion of the graphene layer. The low-energy electron diffraction (LEED) pattern taken after this procedure is shown as inset in Figure 2(a) proving the high crystallinity of the prepared system.

Figure 2: (a) C 1s XPS spectra taken time-dependently during the graphene growth on a Ni(111) surface. The resulting LEED pattern from the prepared graphene layer is shown as inset. (b) 3D presentation of the C 1s XPS profile recorded from graphene growth at 669°C indicating three consecutive development stages: rapid growth, a metastable phase and dissociation of graphene on hot nickel [10].

In Figure 2(b), we present a set of fast XPS spectra taken during the growth of graphene on Ni(111) at 669°C indicating a metastable phase of graphene. The essential point here is that graphene only exists at Ni as long as

carbon is supplied; the graphene peak B at 284.7 eV starts to disappear on a time scale of about 450 s as soon as the carbon supply is cut off. After a short time, this peak is fully gone indicating a clean surface of Ni without any traces of carbon. The nickel substrate is ready again for the next experiment.

Apparently, time-dependent XPS experiments allow to perform a comprehensive study of graphene growth on a metal surface: to disclose all stages of graphene synthesis, to elaborate a solid and reliable protocol aimed to create high-quality graphene layers and even to probe novel metastable phases of graphene at elevated temperatures when construction and deconstruction of graphene coexist [10].

3 Disclosing structural properties of a graphene/metal interface by XPS

XPS can also be efficiently used for characterization of structural properties of a graphene/metal interface [12]. Such systems might be of interest for practical application, for example, in energy storage devices. As a simple example, we will illustrate the successful application of C 1s XPS for disclosing the structure of a graphene/Co(0001) interface. In Figure 3(a), we show the LEED pattern and the structural model for this system. It is assumed that the graphene layer can form two distinct sublattices, marked as C_t and C_h , where C_t carbons are adsorbed on top of the substrate Co atoms, while the other C_h prefer to occupy the hollow sites. The XPS experiment allows to explore this proposition. Figure 3(b) shows two C 1s XPS spectra taken from highly ordered graphene on Co(0001), as confirmed by the LEED pattern. The spectra were recorded at two different photon energies and clearly reveal an asymmetric shape. They can be easily decomposed in two components, C_t and C_h , with identical shapes of ~ 0.4 eV width but different binding energies of 284.9 and 285.17 eV, respectively. The idea behind is rather straightforward. The carbon atoms reside in different crystalline environments due to the aforementioned two preferred positions at the substrate causing an energy shift by different core-hole screening. We need also to point out the different intensities of the C_h and C_t components. The set of C 1s XPS spectra presented in Figure 3(c) taken from this system at different photon energies clearly reveals a systematic variation of PE intensity. This variation is caused by the well-known photoelectron diffraction (PED) effect. It implies a good crystallinity of the studied interface and contains valuable information on the crystal structure of the near-surface atomic layers. The performed analysis unambiguously confirms that only the proposed structural model can lead to the experimentally observed PED pattern [12].

Figure 3: (a) LEED and structural model of single graphene layer on Co(0001) substrate, (b) the C 1s XPS spectra taken from highly oriented graphene on Co(0001), and (c) set of C 1s spectra taken as a function of photon energy.

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4 Lithium interaction with a metal-supported graphene monolayer

Figure 4 demonstrates the change in the electronic structure of a graphene monolayer grown on a Ni(111) thin substrate as the result of thermal decomposition of C_3H_6 gas before and after lithium vapor deposition followed by sample heating at 150°C for 15 min [13]. The C 1s peak of the initial graphene on Ni is shifted by about 0.5 eV to higher BE (Figure 4(a)) as compared to graphite [14] and free-standing graphene [15] indicating a strong coupling of graphene with the metal substrate. Actually, angle-resolved photoemission spectroscopy (ARPES) reveals a shift of the graphene π band at the K point of the Brillouin zone by about 3 eV from the Fermi level to

higher binding energies (Figure 4(b)) due to a hybridization of Ni 3d and C 2p_z orbitals [10, 11]. The deposited lithium suppresses the hybridization thus lowering the π band energy (Figure 4(c)). An upshift of the Dirac point of graphene, where its conduction and valence bands meet, upon lithiation implies an increase of the BE of C 1s electrons by about 0.2 eV as compared to the pristine sample (Figure 4(a)). This value is substantially smaller than the shift of the C 1s peak observed in lithium-intercalated graphite LiC₆ (Figure 4(d)) [16]. The strong asymmetry of the peak in the lithiated graphite is explained by a final-state excitonic screening by the conduction electrons [17]. The position of the C 1s peak and the shape of the high-energy tail are dependent on the lithium intercalation coverage of the carbon sample [18].

Figure 4: (a) Comparison of C 1s XPS spectra of graphene grown on a Ni film before and after lithium vapor deposition. (b, c) ARPES of pristine and lithiated graphene/Ni. (d) Shift of the C 1s peak to higher BE in a LiC₆ XPS spectrum relative to the peak in highly oriented pyrolytic graphite (HOPG).

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In contrast to a Ni substrate, copper interacts only weakly with graphene making graphene/Cu another interesting system for the study of lithium intercalation processes. Figure 5 compares the C 1s XPS spectra measured at a photon energy of 440 eV for monolayer graphene grown on Cu foil before and after the treatment by lithium vapor [19]. The peak position moves from 284.7 to 285.3 eV BE after the lithiation at room temperature. A strong damping of the C 1s signal after the sample treatment evidences the deposition of lithium on top of the graphene/Cu surface. Post-annealing of the lithiated graphene at 300°C for 10 min results in a back-shift of the C 1s peak and a restoration of its intensity. A few reasons were considered to explain this behavior, particularly, lithium desorption or sintering, diffusion of lithium into the Cu bulk or into the graphene/Cu interface during the annealing process. The latter scenario is supported by measuring the XPS Li 1s and Cu 2p lines, as well as the C 1s spectra at different emission angles relative to the sample surface (Figure 5). Based on these results, the authors concluded the necessity of thermal treatment to activate lithium intercalation under the graphene monolayer. This conclusion is in agreement with experiments on lithiation of highly oriented pyrolytic graphite and natural graphite, which have detected a negligible lithium penetration into the bulk of the sample at ambient conditions [16, 20, 21].

Figure 5: C 1s XPS spectra of monolayer graphene on Cu foil before and after lithium vapor deposition with subsequent annealing at 300°C and schematic illustration of the lithium location on the graphene/Cu sample at room temperature and after annealing.

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5 Lithium interaction with few-layer graphene and N-graphene

A possibility of lithium intercalation between graphene layers at room temperature has been observed for polycrystalline graphene samples grown on copper foils (Figure 6(a)), which were then transferred onto SiO₂/Si substrates [22]. The fact that the lithium atoms indeed reached the substrate was demonstrated by the appearance of a component corresponding to the Li_xSiO_y species in the Si 2p XPS spectrum. This result can be explained by the presence of many defects in the graphene domain boundaries, which open pathways for lithium penetration deep into the graphene film.

Figure 6: (a) Scanning electron microscopy images of polycrystalline few-layer graphene and N-graphene grown on Cu foil using the CVD method. (b) C 1s XPS spectra of few-layer graphene (Gr) and N-graphene (N-gr) located on a SiO₂/Si substrate before and after lithium vapor deposition. (c) Change of the N 1s spectrum components of N-graphene after the lithium deposition.

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With the aim to reveal an impact of nitrogen inclusions on the interaction of lithium with graphene, films produced from methane and acetonitrile have been compared. The concentration of nitrogen in N-graphene was about 1.8 at. % as determined from the XPS survey spectrum. While it is commonly accepted that nitrogen improves the performance of carbon materials in lithium-ion batteries, the chemical state of atoms responsible for this improvement is still under discussion [23].

The number of graphene layers in the studied samples was evaluated using the ratio of the intensities and atomic cross-section factors of the C 1s and Si 2p lines. These values introduced in the attenuation law for light photons in matter give about seven layers for the graphene film and four layers for N-graphene. Comparison of the C 1s spectra of the samples before and after lithium deposition (Figure 6(b)) detected an extra shift in N-graphene due to an apparently larger amount of adsorbed lithium. Actually, the XPS spectra collected at a photon energy of 400 eV determined the surface composition of lithiated graphene with stoichiometry LiC₁₄ and N-graphene with LiC₁₀. The fact that the shift of the C 1s line for lithiated N-graphene (0.73 eV) is almost the same as the one for the graphite intercalation compounds with a LiC₆ composition [17] indicates a stronger effect of lithium on the electronic structure of N-graphene.

After lithium deposition, both components of the N 1s spectrum of N-graphene shift to a higher BE (Figure 6(c)). Interestingly, the shift of the component corresponding to pyridinic nitrogen (N_{pyr}) is markedly larger than that for the graphitic nitrogen (N_{gr}) component. As a result, the separation of the two components decreases as compared to the spectrum of the initial sample. Adsorption of lithium modifies the electrostatic potential at the graphene surface, whose value depends on the local surroundings of an atom. A larger modification at graphitic N atoms, where the nitrogen electrons are involved in the joint delocalized π -system of graphene, causes a greater upshift of the N 1s level relative to the Fermi level. Based on these results, we speculate that the incorporation of graphitic N into the graphene layers increases the accumulation of lithium.

6 A step forward: XPS under operation conditions

Ex situ studies provide only part of the information needed since the chemical reactions taking place during operation of solid-gas solid-liquid interface devices result in intermediates and products that most of the time cannot be “quenched” from post-mortem studies [24]. However, since most of the X-ray-based methods require vacuum conditions, they are hardly compatible with gases at atmospheric pressures or liquids. The discrepancy between higher operating pressures applied in catalytic processes and lower measurement pressures accessible during surface characterization is known as the “pressure gap” [25]. The first attempts to bridge the pressure gap were *ex-situ* experiments, where the samples were directly transferred between a reactor and an ultra-high vacuum (UHV) chamber. However, a spectroscopic characterization of the reacting surface under elevated pressure conditions is still challenging due to the attenuation of the incoming X-rays and scattering of the emitted photoelectrons by the gas or liquid molecules under operation conditions. Consequently, the development of new approaches is much needed to overpass the discrepancy between higher pressures required during operation conditions and lower pressures needed for surface characterization.

Siegbahn et al. pioneered the use of a differential pumping stage to reduce gradually the pressure and get the analyzer in a safe pressure range reducing the effective photon-electron path in gas [26]. The next significant advance in this field was achieved by the incorporation of an electrostatic pre-lens system which increased the photoelectron throughput by several orders of magnitude. Ambient pressure XPS (AP-XPS) [27] is a noteworthy advance to close the pressure gap, which uses a small aperture with a differential pumping system to progressively reduce the pressure from the analytic chamber to the analyzer in addition to an electrostatic lens system (to enhance the signal) reaching operation pressures in the mbar range. Thus, AP-XPS has become a growing implemented technique that allows to study surface chemical interactions in more realistic conditions compared to previous studies at UHV. The AP-XPS technique has been extended to higher KE, which is known as hard X-ray photoelectron spectroscopy (HAXPES) [28]. HAXPES brings together the use of smaller aperture nozzles and smaller beam-spot sizes accompanied by the inclusion of a shaped mesh lens to collect high-energy photoelectrons. Higher KE reduce the scattering of photoelectrons increasing the IMFP that the photoelectrons can traverse, before they are completely scattered through the medium, and allow higher operation pressures (up to 100 mbar). Nevertheless, operation at higher excitation energies is challenged by a pronounced reduction in the effective cross section lowering the emission of photoelectrons [29].

A different approach entails the use of transparent membranes based on graphene to separate liquids or gases at elevated pressure from the vacuum side, where the analyzer is placed [30], allowing photoelectron spectroscopy at elevated pressure in the soft X-ray regime. Combining the use of a holey structure with micro-metric holes coated with graphene, the mechanical issue of free standing graphene covering large open areas, while transmitting photoelectrons at low KE, was overcome. Using this approach, it became possible to fabricate an electrochemical liquid flow cell [31] as well as a high pressure gas flow cell [32]. For illustration, Figure 7(a) shows the photoelectron detection scheme for XPS and X-ray absorption spectroscopy (XAS), which can be performed in total electron yield (TEY) or fluorescence yield (FY) mode providing different levels of bulk and surface information. As example, the electrochemical deposition of Co from 4 mM CoSO_4 on graphene was investigated. The deposition of Co was confirmed by *ex situ* mapping by scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy as shown in Figure 7(b). The combined FY and TEY analysis gives insight into the interaction between the electrodeposited Co and graphene. It was found that the deposition of Co onto the graphene layer reduces the cobalt ions from Co^{3+} (bulk, FY spectra) to Co^{2+} (interface graphene/Co, TEY spectra) as shown in Figure 6(c). In addition, Figure 7(d) shows the Co 2p spectra before and after the electrodeposition of cobalt. The peak A is related to the formation of Co^{2+} ions and the peak B to the formation of bounds with oxygen in the form of carbonyl-like species such as $\text{Co}(\text{CO})_x$. Consequently, it was proved that the formation of $\text{Co}(\text{CO})_x$ leads to a reduction of Co^{3+} to Co^{2+} . Furthermore, this approach can be applied with few modifications to the investigation of graphene in contact with Li ions dissolved in a liquid.

Figure 7: (a) Detection scheme. (b) SEM image of a membrane coated with electrodeposited cobalt. Cobalt is magenta and Si is blue. (c) XAS Co L-edge collected in TEY (red) and FY (green) before and during electrodeposition. (d) Co 2p XPS region before (black) and after (red) electrodeposition [30].

7 Summary

All in all, synchrotron-based XPS combined with NEXAFS is powerful tool to probe the physical and chemical transformations occurring in different electrochemical energy-related systems in which carbon materials are widely used as electrode or a component of electrode material. For electrochemistry sp^2 -carbon is the most interesting due to high electrical conductivity. Graphene is the ideal and the most relevant model for this purpose, therefore graphene studies are of great interest to uncover the fundamental processes occurring in broad spectrum electrochemical devices related to energy storage and conversion, such as Li-ion and Li-O₂ batteries, supercapacitors and PEMFCs. Being well-controllable graphene growth is implemented *in situ*, thus providing fine tuning of its properties. PE studies of the model systems composed on graphene help to shed a light on the Li insertion processes, oxygen reduction reactions, etc. The most exciting that single-layer is used as a model electrode transparent for photons and photoelectrons giving the possibility to probe the electrochemical processes in *operando* conditions. We expect that the sharp development of this field will bring us fundamentally new knowledge on electrochemical energy-related systems.

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