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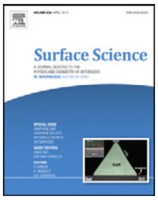

Hydrogenation and dehydrogenation of nitrogen-doped graphene investigated by X-ray photoelectron spectroscopy

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ABSTRACT

We studied the hydrogenation and dehydrogenation of nitrogen-doped graphene (NDG) by in situ high-resolution X-ray photoelectron spectroscopy (XPS) and temperature-programmed XPS (TPXPS). Nitrogen-doped graphene was prepared by low energy nitrogen implantation in pristine graphene on Ni(111). Hydrogenation of NDG was performed by exposure to atomic hydrogen. Upon hydrogenation the XP spectra in the C 1s region reveal one new peak, shifted to lower binding energies as compared to graphene, which is associated with newly formed CH groups. In the N 1s region two new peaks, shifted to higher binding energies are observed; these are associated with hydrogenated pyridinic and graphitic nitrogen. TPXPS spectra reveal a different thermal stability of the two hydrogenated nitrogen species, while the C–H groups of graphene show no significant changes compared to undoped hydrogenated graphene.

1. Introduction

Graphene, a 2D material consisting of honeycomb arranged sp^2-hybridized carbon atoms, has gained significant interest over the last years, due to its unusual physical and chemical properties [1,2]. These include a high charge carrier mobility [3], due to its linear dispersion at the Dirac point [4], its high transparency [5], which makes it a potential candidate as a replacement for indium tin oxide in modern display technology. Its inertness [6] and impermeability [7] are some of its outstanding chemical properties; in this context, applications as membrane, and for corrosion protection [8,9] as well as for gas separation [10,11] and detection [12] are discussed.

One other important application of graphene, often discussed in literature, is as a potential hydrogen storage material [13]. Due to its unsaturated carbon backbone, it is possible to attach one hydrogen atom to every carbon atom of graphene, yielding exclusively sp^3-hybridized carbon atoms. The resulting material is denoted as graphane (C_nH_n) and has a high hydrogen storage capacity [14,15]. In case of hydrogenation of supported graphene, i.e., of a graphene layer adsorbed on a solid surface, the achievable degree of hydrogenation depends on the surface and the specific interaction between graphene and the surface: For graphene on SiO_2/Si 17% of carbon atoms can be hydrogenated [16]; for hydrogenation with molecular hydrogen on Ir(111) intercalation is found, and the intercalated hydrogen can react with graphene [17]. On Ni(111), hydrogenation of 50% of the carbon atoms is found (at sufficiently high exposure to atomic hydrogen), resulting in single-side hydrogenated graphene; in this so-called graphone ($C_nH_{n/2}$), the non-hydrogenated carbon atoms strongly interact with Ni surface. If gold is intercalated between Ni(111) and graphene, only 25% of the carbon atoms bind hydrogen [18]. For a potential application, in addition to a high storage capacity also a sufficiently low release temperature of hydrogen, preferably close to room temperature is required. Furthermore, the hydrogen storage and release processes should be fully reversible, i.e., no loss of carbon should occur, as this would deteriorate the storage material and also could poison a hydrogen fuel cell.

To tune the electronic and chemical properties of graphene, doping and chemical modification have been proposed as two suitable pathways. Doping of graphene can induce a band gap that is crucial for applications in the semiconductor industry. The neighbors in the periodic system of elements, nitrogen and boron, are the natural candidates for such a chemical doping, and we herein will focus on nitrogen-doped graphene (NDG). NDG has already received considerable attention [19–21], and applications in ultra-capacitors and lithium ion batteries, electrochemical biosensing, and as metal-free electrocatalyst for oxygen reduction in fuel cells [22–25] have been proposed in literature. Furthermore, also the chemical reactivity of the dopants is of interest, as covalent doping-sites in graphene could serve as potential anchor points for further functionalization.

Herein, we investigate the hydrogenation and dehydrogenation of nitrogen-doped graphene supported on Ni(111) by in situ high-resolution photoelectron spectroscopy. In the past, this method has proven to be very powerful to characterize the preparation of nitrogen-doped graphene on the one hand [20,26] and the hydrogenation of undoped graphene on the other hand [27,28]. Herein, we present the first study addressing the hydrogenation of nitrogen-doped graphene. From the analysis of the C 1s and N 1s spectra during heating of a

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hydrogenated layer detailed information on the hydrogenation and dehydrogenation is obtained. In particular, the differences between the hydrogenation of different nitrogen species, i.e. graphitic and pyridinic nitrogen are evaluated.

2. Experimental setup

The experimental setup consists of a two-chamber ultra-high vacuum apparatus [29]. The preparation chamber is equipped with a LEED system, an atomic hydrogen source, dosing facilities and a sputter gun. The analyzer chamber contains an Omicron EA 125 electron analyzer, a multicapillary array doser and a supersonic molecular beam. The sample can be transferred between the two chambers with a manipulator, which allows for XYZ motion, tilting and rotation. The temperature is measured by a type K thermocouple spot welded directly onto the side of the crystal. All XP Spectra were recorded at BESSY II of the Helmholtz-Zentrum Berlin. The beamline used was U49/2 PGM-1. All binding energies are calibrated to the Fermi level. We did not find any alteration of the sample by the synchrotron light. The Ni(111) crystal was cleaned by repeated cycles of annealing to 900 K and sputtering. Graphene was prepared at 900 K using propylene as precursor, dosed directly onto the sample using the molecular beam [30–32]. The partial pressure of propylene on the sample during preparation was approx. 2×10^{-6} mbar. Doping is achieved by bombarding graphene with low energy nitrogen ions using the sputter gun. The doping process is described in detail elsewhere [19]. The dinitrogen partial pressure during doping was 5×10^{-6} mbar, the ion current on the sample was approx. 350 nA, and the sample temperature below 170 K. The kinetic energy of the nitrogen ions was 50 eV. The samples were sputtered for 10 min, yielding N amounts between 0.027 and 0.045 ML as was determined for each preparation by XPS. These amounts are very similar to values obtained in earlier work under similar conditions [19]. As the overall amount of N is very low, and varies slightly from experiment to experiment, as discussed above, we use the fractions of hydrogenated nitrogen species to describe the degree of hydrogenation throughout this paper, with the absolute amounts denoted in the figure captions. The hydrogenation of graphene was achieved by using atomic hydrogen from a dihydrogen (H_2) cracking source. The background H_2 pressure in the chamber during hydrogenation was between 1×10^{-7} and 5×10^{-7} mbar, depending on the desired exposure. As the sample was close to the hydrogen source, the absolute pressure of atomic hydrogen differs from the values given.

3. Results and discussion

3.1. Hydrogenation of carbon in nitrogen-doped graphene

When dosing atomic hydrogen onto NDG, both the carbon and the nitrogen species react, and subsequently a variety of new species are identified in the C 1s and N 1s spectra. The behavior in the C 1s spectra largely mimics the behavior found for undoped graphene on Ni(111), which has been reported on in great detail recently; see [27]. As we herein focus on the reactivity of the dopant atoms in nitrogen-doped graphene, we will restrict the discussion of the C 1s spectra to one typical measurement, which is shown in Fig. 1. The spectrum at 180 K in Fig. 1a (black) has been collected after exposing NDG to 90 L atomic hydrogen. In addition to the signal of pristine graphene at 284.9 eV, a new H-induced species is found at 284.4 eV; its binding energy is in good agreement with the value of 284.3 eV found for hydrogenation of pristine graphene. This signal stems from sp^3-hybridized carbon atoms to which the hydrogen is bound. After the adsorption experiment, dehydrogenation was studied by applying a constant temperature ramp, while continuously measuring XP spectra, i.e. by performing a temperature programmed XPS experiment. Spectra at selected temperatures are show in Fig. 1a, and the complete data set is shown in Fig. 1b in a color-coded density plot. The quantitative analysis obtained by peak-fitting this experiment is depicted in Fig. 1c. Upon heating, characteristic changes are observed in the XP spectra that are assigned to a stepwise dehydrogenation yielding gaseous H_2. The spectrum at 650 K is identical to that of the surface prior to exposure to hydrogen, reflecting the reversibility of the hydrogenation/dehydrogenation process. The rate maxima, i.e. the H_2 desorption temperatures, are determined from the inflection points of the decrease of the hydrogenated graphene signal (which goes along with the increase of graphene signal) in Fig. 1c, to be at 330 and 600 K. We thus observe stepwise dehydrogenation, at two characteristic temperatures, very similar to the behavior during the dehydrogenation of hydrogenated undoped graphene [27]. The similarity also holds for the hydrogen coverage of 0.9 ± 0.1 ML, which, within the error bars of the experiment and the fitting procedure, is identical to the value found for undoped graphene (1.1 ± 0.1 ML) at the same exposure.

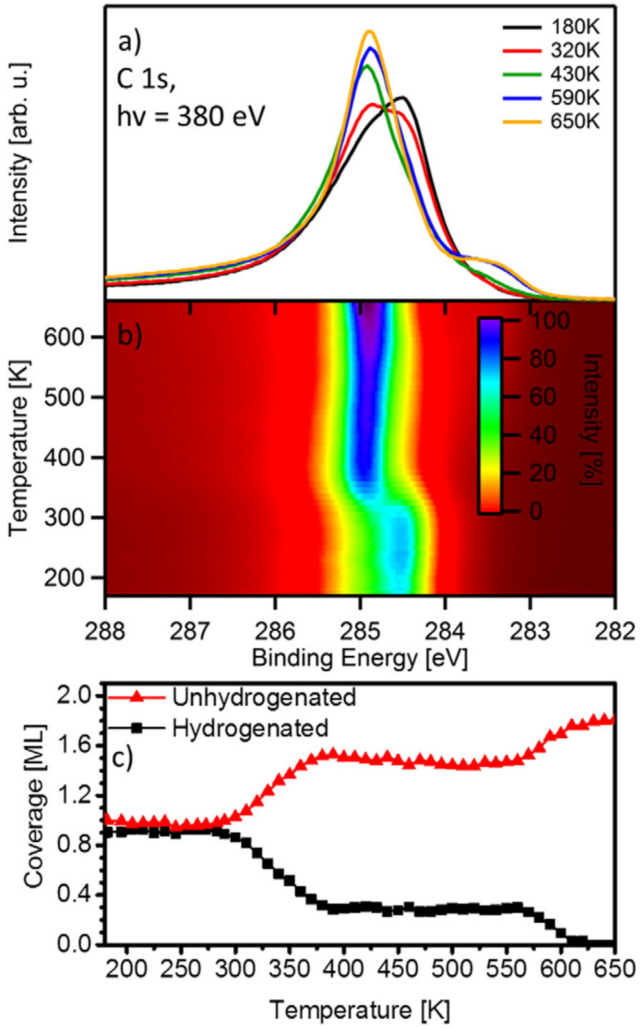

Fig. 1. TPXPS experiment in the C 1s core level of NDG ($\Theta_N = 0.029$ ML) exposed to 90 L atomic hydrogen. a) Selected spectra recorded at characteristic temperatures; b) color-coded density plot of full data set; c) quantitative analysis of the experiment. The signal due to carbidic carbon (~283.5 eV) is not shown.

Interestingly, we do not observe any new species in the C 1s core level region as compared to hydrogenated undoped graphene. This may be due to the low concentration and a similar binding energy of new components such as C–N–H groups that are formed. Furthermore, we observe no irreversible effects that the hydrogenation might have on graphene, e.g. binding energy shifts, due to altering the graphene substrate interactions, or loss of carbon due to etching,