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# Reversible photon-induced oxidation of graphene by $NO_2$ adsorption

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ABSTRACT

We show that an oxidized graphene sheet is formed by $NO_2$ adsorption and subsequent photodissociation, through an analysis of X-ray absorption and photoemission spectroscopic results. Adsorption of $NO_2$ on graphene grown on Ir(111) leads to a strong rehybridization of the unoccupied $\pi^*$ states and the appearance of new features in the C 1*s* core level line. This is a reversible process, such that pristine graphene can be recovered by thermal treatment. The formation of oxidized graphene is sensitive to the photon-flux, resulting in an intermediate phase of oxidized graphene. Our results provide an interesting pathway towards lithographic patterning processes in graphene.

## 1. Introduction

The influence of ambient species is of great importance for the widespread use of graphene in technology, and this topic has thus received considerable attention in recent years [1–5]. Many molecules exhibit only a weak adsorption bond to graphene; the polar molecules, $H_2O$ and $NH_3$ may serve as examples [6,7]. As a consequence, they are molecularly adsorbed with no sign of dissociation, not even under the influence of ultraviolet (UV) radiation. Molecular oxygen itself is reported to only intercalate between graphene and Ir(111) with no sign of chemical interaction [8]. $NO_2$, on the other hand, is more strongly adsorbed, as judged from experimental data for adsorption on carbon nanotubes [9], and its dissociation under photon irradiation is well known [10–12]. The preparation of oxidized graphene sheets has so far been achieved by either a strong physical or chemical treatment such as oxygen atom bombardment [13], or dispersion of graphite oxide in basic solutions, yielding what is expected to be a precursor to graphene preparation [14]. Considering this precursor application of oxidized graphene (we will refer to this in the following as graphene oxide, GrO), the quality of the GrO layer has been reported to be essential for the thermal recovery of graphene [15]. The authors show that the thermal recovery of graphene reveals the highest quality for low oxygen coverages in GrO, consisting of mainly epoxidic oxygen atoms, while other oxide phases destroy the graphene backbone. Here we provide an alternative and less intrusive pathway for GrO preparation, by $NO_2$ adsorption and subsequent dissociation under UV irradiation, which induces a transformation of graphene into GrO, consisting of mainly the favored epoxidic oxygen atoms and fewer defects on graphene. We explain the observed results in the context of a simple photon-induced oxidation mechanism.

## 2. Experimental details

The photoemission spectroscopy (PES) and near-edge X-ray absorption fine structure (NEXAFS) measurements were performed at the UE56/2-PGM-1 and PGM-2 beamlines of the BESSY II synchrotron radiation facility, Berlin (Germany). Graphene was prepared on a clean Ir(111) single crystal surface. The cleaning process consisted of subsequent cycles of thermal flashing up to 1800 °C followed by annealing at an oxygen partial pressure of $1 \times 10^{-6}$ mbar at 1300 °C. Graphene on Ir(111)was prepared by thermal decomposition of ethylene at 1250 °C at a partial pressure of $1 \times 10^{-6}$ mbar. The quality of the graphene/Ir(111) sample was verified by means of low energy electron diffraction (LEED) and core-level as well as valence-band photoelectron spectroscopy. The adsorption of high purity $NO_2$ was performed at a partial pressure of $p = 5 \times 10^{-8}$ mbar and a sample temperature of 100 K. The temperature was kept constant for all following measurements, unless declared otherwise. NEXAFS spectra were collected at the carbon *K* and oxygen *K* absorption edges in the surface sensitive partial electron yield mode (PEY) using a hemispherical detector and Auger electron yield. The base pressure during measurements was better than $7 \times 10^{-11}$ mbar.

## 3. Results and discussion

Fig. 1 shows a set of photoemission (PE) survey spectra of graphene/Ir(111), starting with the pristine graphene surface and stepwise exposure of $NO_2$ up to 1400 L, recorded at 800 eV photon energy and an average flux of approx. $10^{11}$ photons/s and a total photon dose of

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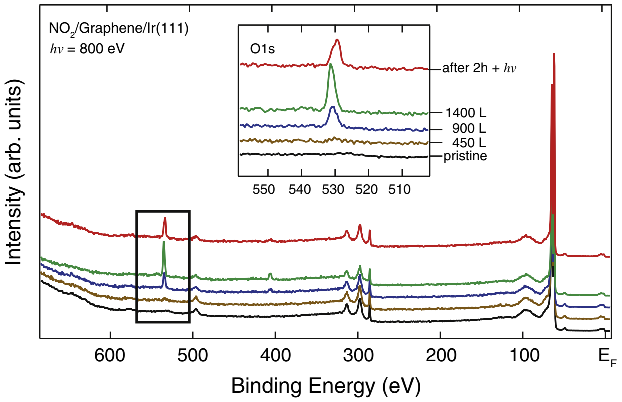

**Fig. 1.** PE overview spectra for the $NO_2$ deposition on graphene/Ir(111). Each spectrum represents a specific dose starting from pristine graphene. The inset shows a zoom on the O 1*s* core level component. Upon irradiation, the N 1*s* line vanishes and the O 1*s* core level line is shifted to lower binding energy, implying a change of the chemical environment of the oxygen atoms.

approx. $10^{14}$ photons. The flux and flux densities presented in the following are calculated according to the beamline characteristics from Ref. [16]. The fifth spectrum from the bottom shows the PE survey spectrum after approximately 2 h further irradiation at 450 and 800 eV photon energy. All features of the spectrum can be ascribed to either iridium or carbon and are in agreement with the literature [13,17,18]. At around 410 and 530 eV binding energy the N 1*s* and O 1*s* core level lines appear upon dosage of $NO_2$. The core level lines reflect the increase of the amount of adsorbed $NO_2$ as expected. The O 1*s* and N 1*s* levels show a ratio of approx. 4:1, which corresponds to a ratio of two oxygen atoms per nitrogen atom, taking into account the photoemission cross sections for the nitrogen and oxygen 1*s* lines excited by 800 eV photons [19]. After exposure of the sample to light of photon energies between 450 and 800 eV (last spectrum in the row after a total dose of approx. $10^{15}$ photons) the N 1*s* core level component almost completely vanishes, while the O 1*s* core level is shifted to lower binding energies. We assign this fact to a breakup of the adsorbed molecule, with concomitant nitrogen desorption. The shift of the O 1*s* core level line between the fourth and fifth spectrum implies a change of the chemical environment of the oxygen atom from adsorbed $NO_2$. We interpret this as a decomposition of $NO_2$, leaving atomic oxygen as a reactant on the surface. This decomposition is apparently induced by the soft X-rays, not unexpectedly since the decomposition of $NO_2$ in the gas phase starts already at 400 nm (3 eV photon energy) [10,11] and adsorbed on surfaces at 193 nm or 6.5 eV photon energy [20], but may be also induced by secondary electron-induced decomposition.

Evidence for a chemical reaction of graphene with the oxygen atoms present on the surface can be found in the photoemission data from the graphene/Ir(111) substrate. Consider the C 1*s* core level line in Fig. 2 and the Ir $4f_{7/2}$ core level line in Fig. 3. In Fig. 2 the formerly sharp C 1*s* core level line (see the inset) exhibits an additional shoulder approx. 500 meV towards higher binding energy, and a new feature at 286.2 eV binding energy upon $NO_2$ adsorption. This component is usually ascribed to graphene oxide [13,21–23]. In fact, it is possible to assign specific adsorption sites of the oxygen atoms to the core level line components [13]. In bulk graphite oxide, different oxygen adsorption sites may occur: Hydroxyl groups (C–OH), ketones (C═O), esters (C–O–C without a C–C bond) and epoxidic oxygen (C–O–C with a C–C bond) [14,24]. In principle these functional groups also appear in graphene oxide sheets [22,23]. In a recent study of oxidized graphene prepared by atomic oxygen exposure, Vinogradov et al. interpreted their findings in terms of mostly epoxidic oxygen formation on graphene/Ir(111) [13]. Our observation of two new C 1*s* line components, one at 286.2 eV binding energy and a shoulder around 500 meV higher binding energy apart from the main graphene C 1*s* peak, matches perfectly with their analysis of the formation of an epoxidic oxygen moiety on graphene. The shoulder at 284.6 eV binding energy is assigned to the carbon atoms adjacent to the epoxidic carbon atoms. Due to rehybridization, these neighboring atoms are now able to bind more strongly to the Ir(111) substrate, e.g. are pinned (following the nomenclature of Feibelman in Ref. [25]) to the surface iridium atoms [13,25]. From the best fit of the C 1*s* core level lines, using a polynomial background and Voigt profiles with restricted Lorentzian weights, we are able to quantify the amount of oxidized carbon atoms on the surface. The intensity of the pristine C 1*s* line is split into roughly 38% remaining sp$^2$ carbon, 23% epoxidic carbon and 39% sp$^3$ hybridized carbon atoms in the oxidized spectrum. Note that the FWHM for components B and C are equal but differ for the sp$^2$ component. This

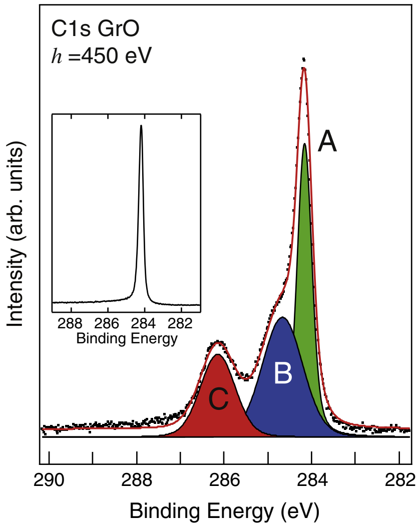

**Fig. 2.** C 1*s* core level photoemission spectrum for graphene oxide. The components of the fit are (A) sp$^2$-bonded carbon from graphene, (B) sp$^3$ rehybridized carbon neighboring the epoxidic carbon atoms and (C) epoxidic carbon atoms. The inset shows the pristine graphene/Ir(111) C 1*s* core level line.

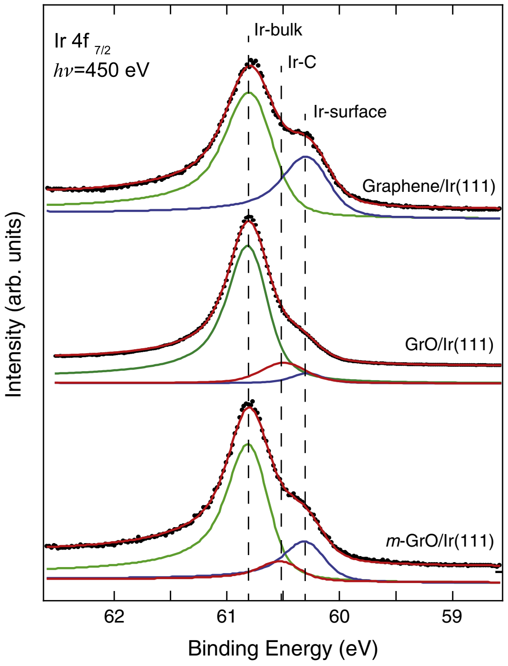

**Fig. 3.** PE spectra from the Ir $4f_{7/2}$ core level as observed for pristine graphene/Ir(111), completely oxidized graphene oxide (GrO) and metastable graphene/Ir(111) (*m*-GrO). The fitted spectral lines are the Ir 4*f* bulk component (green), the surface component (blue) and the Ir–carbon signal (red).