



NEXAFS Anisotropy of Molecular Excitations Preceding the Carbon Continuum Edge in CVD Graphene on Copper

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In chemical-vapour-deposited graphene on copper, four molecular excitations have been observed between the π^* - and σ^* -resonances with near-edge x-ray absorption fine structure spectroscopy, which we assign to hydroxyl, carbonyl, epoxide and carboxyl moieties. In general, the associated bonds have an isotropic distribution of orientations.

1. Introduction

Since the isolation of graphene [1], significant development of graphene-based technology has occurred [2, 3]. Chemical-vapour deposition (CVD) of graphene is a promising candidate for industrial-scale synthesis of the material. Future device applications of graphene will depend on surface quality. Thus there is considerable effort to understand the properties of surface adsorbates.

Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy is a surface-sensitive tool to investigate the electronic structure of materials at and near the surface. With this technique, the orientations of particular bonds can be probed using linearly polarised synchrotron light. NEXAFS has successfully been applied to graphene [4] and also to characterise molecular excitations in graphene oxide [5-8]. However, the anisotropies, if any, of molecular excitations associated with carbon bonds in graphene are not well established.

In this work, NEXAFS data were recorded for graphene on copper foil substrates. The energy range of the incident x-rays spanned the carbon 1s edge. In addition to the expected π^* - and σ^* -resonances a number of molecular excitations have been identified at energies just below the carbon absorption edge. Importantly, the angular dependences of these excitations have been determined and analysed.

2. Setup and Method

The graphene on copper samples investigated were grown with effectively the same CVD method, but in two different furnaces, in order to exclude possible effects due to the deposition process. Two samples were synthesized at Kyung Hee University [3] (labelled K1 and K2) and two others were obtained commercially from Graphenea [9] (labelled G1 and G2). K2 had a PMMA protective layer, which was removed with acetone and isopropanol prior to the measurement. For consistency the G2 sample was treated in the same way despite it not having the PMMA layer. Scanning electron microscopy showed that the Graphenea samples had a more pronounced surface topography.

NEXAFS measurements were performed at the soft x-ray beam line at the Australian Synchrotron [10]. Linearly polarised light with a spectral resolution $E/\Delta E = 6000$ at 300 eV was scanned across the carbon K-edge, spanning the energy range 280 eV – 320 eV. Angle-dependent measurements were made by tilting the sample with respect to the beam direction



and thus varying the glancing angle θ , defined as the angle between the incident beam and the sample surface.

3. Results

The NEXAFS data recorded at different angles θ for the samples K1, K2, G1 and G2 are shown in Figs. 1(a-d), respectively. All four samples show a pronounced π^* -resonance at 285 eV and σ^* -resonances at 292 eV. As expected, the π^* -intensities increase as the glancing angle θ decreases and for the σ^* -intensities this is vice-versa.

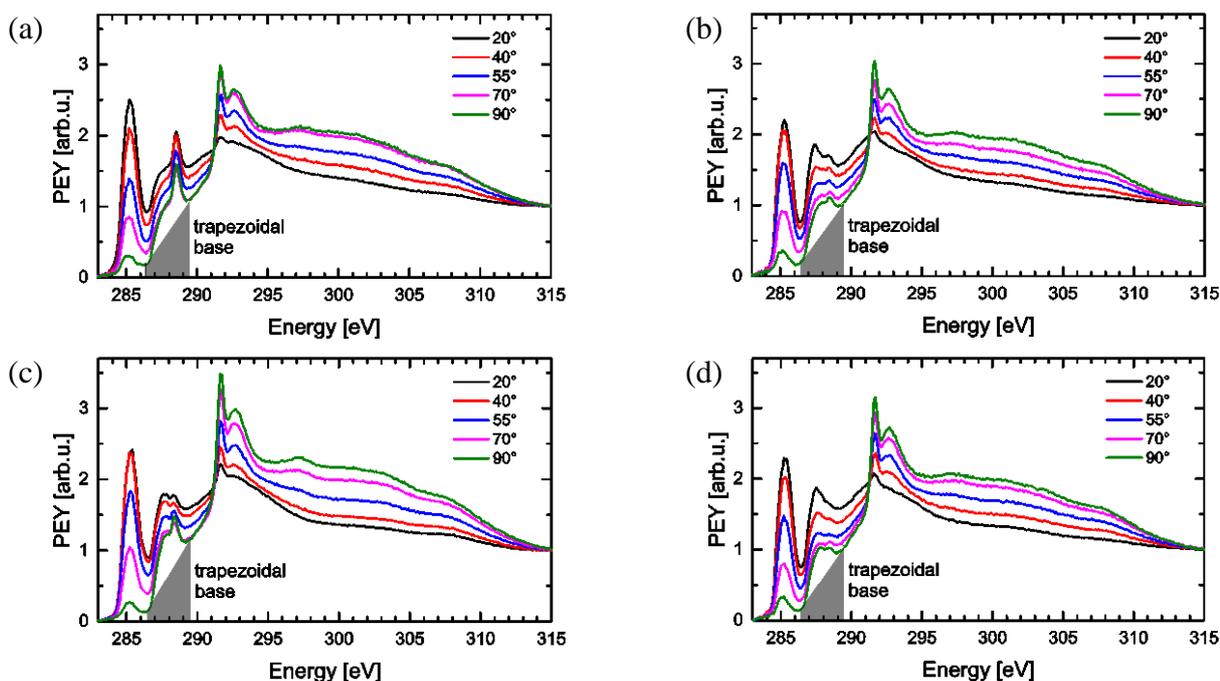


Fig. 1. Angle-dependent NEXAFS spectra for graphene on copper for (a) K1, (b) G1, (c) K2 and (d) G2, respectively. The shaded trapezoids indicate the background subtraction applied in the least-square fits for $\theta = 90^\circ$, see text.

Located between the π^* - and σ^* -resonances, molecular excitations of varying intensities are observed that precede the carbon absorption edge. The spectral features of these intermediate excitations appear on top of a background of intensity associated with delocalised π^* - and σ^* -orbitals. These intermediate excitations correspond commonly to surface adsorbates, in particular those containing oxygen and hydrogen [11].

Partial spectra and fits for the intermediate energy region 286.5 eV – 289.5 eV are shown in Figs. 2 (a-d) for a glancing angle $\theta = 20^\circ$. The measured spectra have been subtracted using the background intensity as approximated by trapezoids and illustrated in Fig. 1 for $\theta = 90^\circ$. Spectra for the other angles were treated equivalently. In these fits, the mean energy and the FWHM of each Gaussian was kept constant, whereas the amplitude was a free parameter. The four mean energies of the Gaussians may be associated with distinct moieties, i.e. with hydroxyl C-OH (287.0 eV [7]), carbonyl C=O (287.4 eV [5]), epoxide C-O-C (287.9 eV [8]), carboxyl –COOH (288.5 eV [8]), respectively.

The fits provide quantitative insight into the angular dependence of the four molecular excitations which permits the identification of the average bond orientation. The area of the Gaussians is plotted as a function of $\cos^2(\theta)$ (Insets of Fig. 2). No orientation anisotropy is



observed for the epoxide C-O-C (287.9 eV) and carboxyl -COOH (288.5 eV) moieties, since the associated intensities do not vary with $\cos^2(\theta)$.

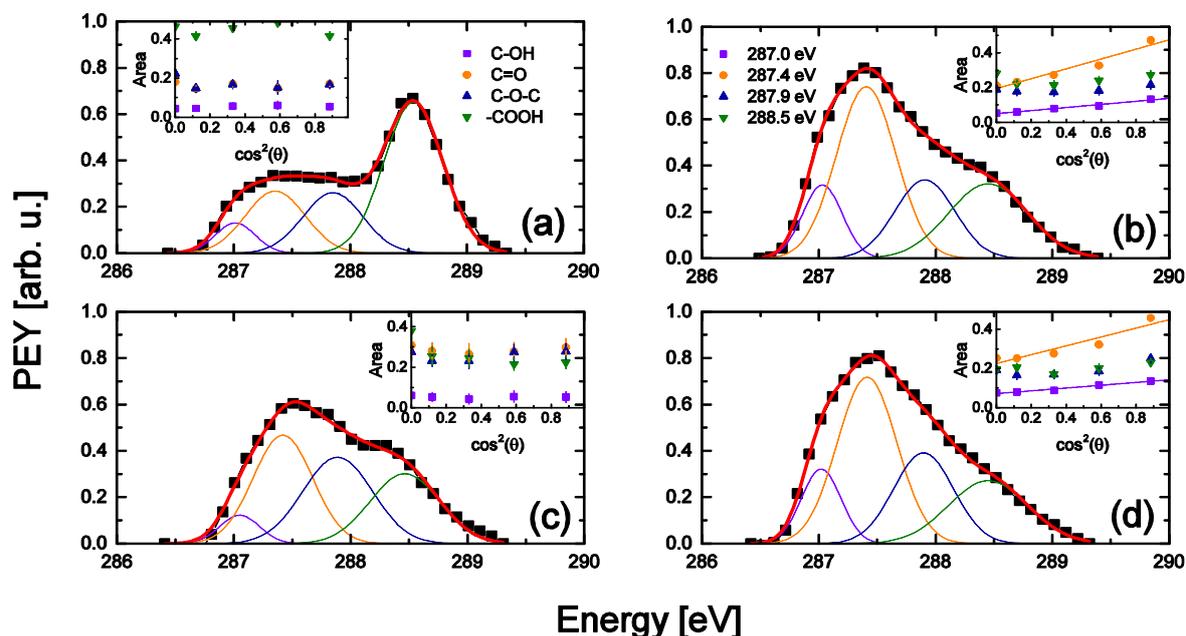


Fig. 2. Background-subtracted partial NEXAFS spectra of the partial electron yield (PEY) at $\theta = 20^\circ$ showing the structures due to molecular excitations preceding the carbon-edge for (a) K1, (b) G1, (c) K2 and (d) G2, respectively. The inset shows the angular dependence of each excitation using the same colour scheme as indicated in the legends. The legend in (a) gives the associated chemical groups and the legend in (b) the corresponding excitation energies, respectively. Lines are least-square fits to determine the dichroic ratio.

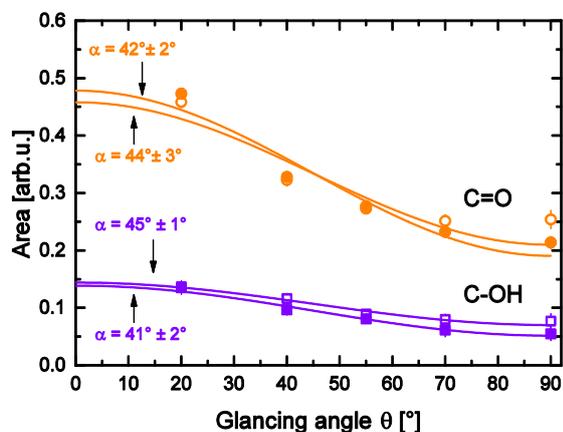


Fig. 3. Measured peak areas plotted as a function of glancing angle θ for the two anisotropic bonds C-OH and C=O of sample G1 (solid) and G2 (open) and least-squares fits.

In the figure the angular dependencies of the measured intensities have been fitted with the analytical expression expected for linearly polarised incident light, as detailed in [12]. Results indicate average tilt angles of $\alpha = 41^\circ$ and 45° for C-OH and 42° and 44° for C=O, respectively. For both samples, these tilt angles are agree with the extracted DR values, given above.

The observed tilts for C-OH and C=O away from normal orientation with respect to the surface may be because in addition to many molecular groups with orthogonal orientation, in

In contrast, for G1 and G2, but interestingly not for K1 and K2, the intensities of the C-OH and C=O excitations increase with increasing angle. For these two cases a least-squares fit gives the dichroic ratio (DR), as defined in [4], which represents the average degree of non-isotropic alignment of a bond orientation; $DR = -1$ indicates orthogonal orientation of the bond of a moiety with respect to the surface, whereas $DR = 0$ represents an on-average isotropic bond orientation. For the G1 and G2 samples the C-OH and C=O moieties have $DR = -0.42$ and -0.46 and $DR = -0.33$ and also -0.33 , respectively.

Figure 3 shows a more detailed analysis of the bond orientation of the C-OH and C=O moieties based on data for samples G1 and G2.



these two particular samples a significant number is oriented randomly. This may occur at grain boundaries, suggesting that for these samples the hydroxyl and carbonyl moieties are more common there than epoxide and carboxyl groups.

4. Conclusions

Our preliminary results identify four distinct excitations preceding the carbon 1s edge that are typically present in CVD graphene on copper, which occur at energies of 287.0 eV, 287.4 eV, 287.9 eV and 288.5 eV, respectively. These hydroxyl, carbonyl, epoxide and carboxyl moieties are typically oriented isotropically. An exception has been observed on two samples for C-OH and C=O bonds for which an average tilt angle of $\alpha = 43^\circ$ has been determined, which may be due to a significant presence at graphene grain boundaries with random orientation.

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