

Supporting Information

Atomic Oxygen on Graphite: Chemical Characterization and Thermal Reduction.

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1 Core level analysis

For the C1s spectrum measured on the pristine HOPG surface we found binding energy (BE) of 284.35 eV, Lorentzian width $\Gamma_L=0.13$ eV, Gaussian width $\Gamma_G=0.16$ eV and asymmetry $\alpha=0.08$.

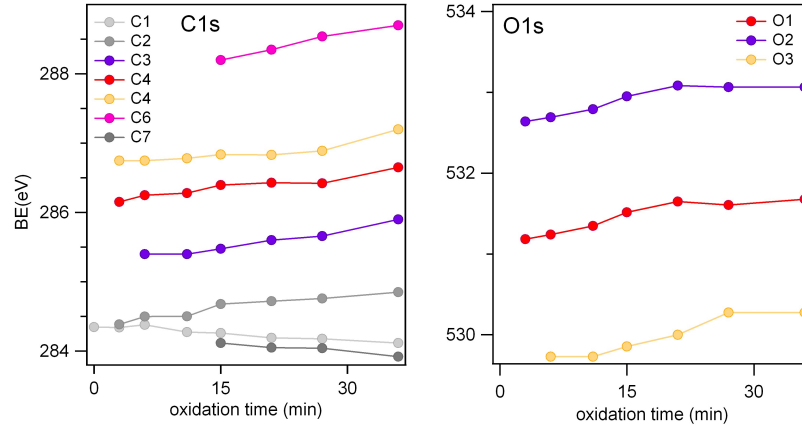


Fig.S 1: Binding energy positions of the C1s and O1s spectral components (see Fig.1) as a function of the oxidation time.

In the analysis of the C1s spectra measured on the oxidized HOPG, for C1 we fixed Γ_L and α at the values obtained for the clean HOPG, whereas Γ_G , left as a free parameter, increased up to 0.28 eV. For the C2-C7 components the Gaussian widths were largely dominating over Γ_L and increased from 0.4-0.5 eV to 1.0-1.5 eV with oxidation time. The BE positions found for the C1s and O1s core level components are plotted in Fig.S1 vs. the oxidation time.

2 Estimation of the oxygen coverage

A very rough estimation of the oxygen coverage can be obtained for the sample oxidized for 3 minutes. In this case by neglecting the minute amount of ethers appearing in the O1s spectrum, the HOPG surface can be considered as divided into the fraction ν containing the C atoms directly bonded to epoxy O atoms and the remaining bare fraction $(1-\nu)$. The first HOPG layer contributes to the component C4 in the area ν and to the components C1 and C2 in the area $(1-\nu)$, whereas the layers below the first, that contain only C-C bonds, contribute exclusively to C1. In the region ν the signal is screened by the presence of the O atoms.

Therefore in the bare region the photoemission signal is given by¹

$$I'_{sp^2} = I_0 \sum_{n=0}^{\infty} \exp\left(\frac{-nd_{GR}}{\lambda \cos\theta}\right) = I_0 \frac{1}{1 - \exp\left(\frac{-d_{GR}}{\lambda \cos\theta}\right)} \quad (1)$$

where $I_0 = N\sigma$, being N the number of C atoms per surface area and σ the C1s photoionization cross section, λ is the escape depth of 120 eV kinetic energy photoelectrons, d_{GR} is the monolayer thickness of graphite and θ is the angle between the surface normal and the axis of the electron analyzer.

In the ν region below the epoxy oxygens the photoemission signal of the first graphite layer is given by

$$I_{ep} = I_0 \exp\left(\frac{-d_{ep}}{\lambda \cos\theta}\right) \quad (2)$$

where $\exp(-d_{ep}/\lambda \cos\theta)$ is the attenuation factor due the epoxy layer, whereas the signal of the HOPG layers below the first one is

$$I''_{sp^2} = I_0 \exp\left(\frac{-d_{ep}}{\lambda \cos\theta}\right) \sum_{n=1}^{\infty} \exp\left(\frac{-nd_{GR}}{\lambda \cos\theta}\right) = I_0 \exp\left(\frac{-d_{ep}}{\lambda \cos\theta}\right) \frac{1}{\exp\left(\frac{d_{GR}}{\lambda \cos\theta}\right) - 1} \quad (3)$$

Therefore the ratio R between the intensity of C4 and the sum of C1 + C2 is

$$R = \frac{I_{C4}}{I_{C1+C2}} = \frac{\nu I_{ep}}{(1-\nu) I'_{sp^2} + \nu I''_{sp^2}}. \quad (4)$$

By using $\lambda = 6 \text{ \AA}$,² $d_{GR} = 3.35 \text{ \AA}$, $d_{ep} = 1.22 \text{ \AA}$ and calculating R from the data of Fig.1, ν results to be 0.24. Thus the coverage of the epoxy O atoms is $\theta_{ep} = 0.12 \text{ ML}$, (1ML=1 monolayer= $3.8 \times 10^{15} \text{ atoms/cm}^2$). In this calculation we have taken into account only epoxy groups, as indicated by the C1s spectrum. Indeed, the corresponding O1s spectrum shows also a minute ether component and therefore we assumed that at $t_{ox}=3$ minutes the total O coverage is approximately $\theta \simeq 0.14 \text{ ML}$. The intensities of the O1s spectra at $t_{ox}=3$ and $t_{ox}=36$ minutes were used to estimate the total O coverage after the last strong oxidation, which resulted to be $\theta \simeq 0.54 \text{ ML}$. It must be noted that these numbers are only very approximate evaluations of the effective coverage because the screening due to epoxides might be different from that of in plane ethers and of semiquinones and, more important, the component intensity can be significantly influenced by diffraction effects.

3 Valence band

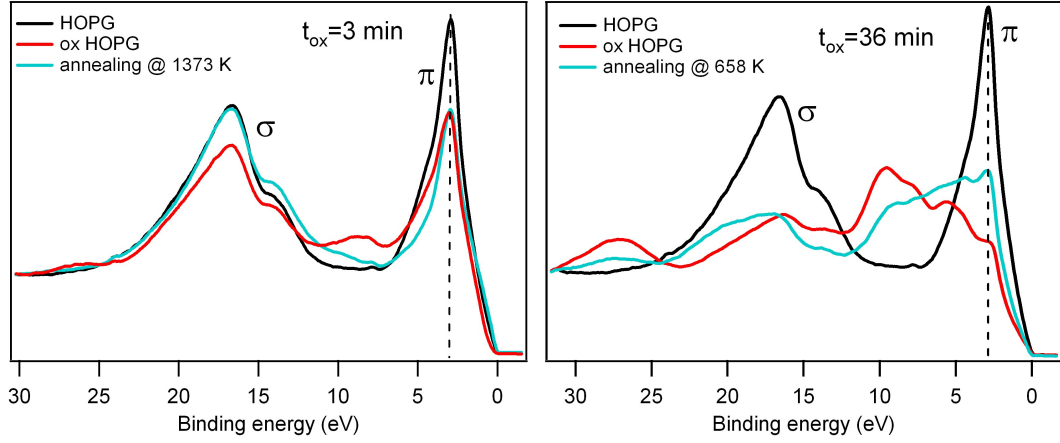


Fig.S 2: Valence band spectra measured at photon energy of 130 eV and at emission angle of 20° on the HOPG surface (left) oxidized for 3 minutes before and after thermal annealing at 1373 K and (right) oxidized for 36 minutes before and after thermal annealing at 658 K. The VB spectrum measured on the pristine HOPG is also shown in each panel. The curves in the left panel show that for the softly oxidized sample the intensity of the π band is not completely retrieved after high temperature annealing. In the other case the curve measured after annealing at 658 K shows that the complete loss of the epoxy groups (compare Fig.5) does not correspond to a substantial recovery of the π band which is still strongly attenuated by the presence of defects and O saturated vacancies, that ruin the π conjugation.

4 Oxygen coverage

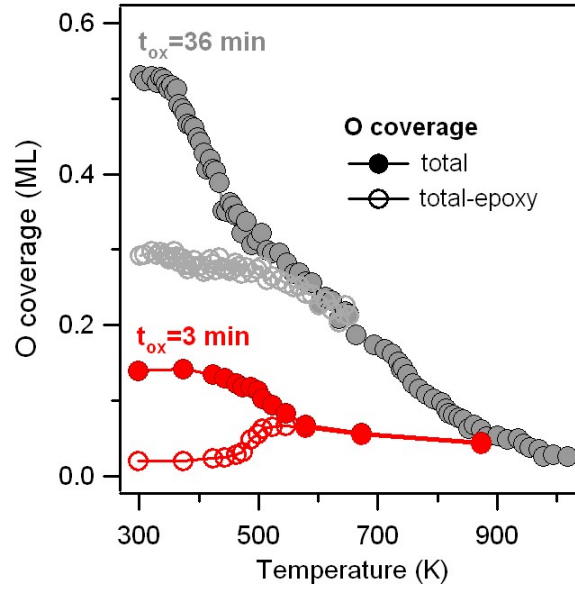


Fig.S 3: Oxygen coverage vs. annealing temperature as measured for the HOPG surface oxidized for 3 and 36 minutes

5 References

¹R. Memeo et al. *Thin Sol. Films* **159**, 109, (1983)

²F. Himpsel et al. *Phys. Rev. B* **38**, 6084 (1988)