Electronic Supplementary Information

The influence of intercalated oxygen on the properties of graphene on polycrystalline Cu under various environmental conditions


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Si Table 1: Procedures for T-R-cycling of MLG, FLG and GF samples presented in this work. All heating and cooling steps were performed in vacuum.
SI Figure 1: Raman spectra of GF flakes as loaded (bottom), three times T-R-cycled and subsequently exposed to air (middle) and five times T-R-cycled and subsequently exposed to air (top). Relevant peaks of Cu oxide are located at shifts < 1000 cm$^{-1}$. Peaks related to graphene are denoted as D at 1355 cm$^{-1}$, G at 1589 cm$^{-1}$ and 2D at 2688 cm$^{-1}$.

While the Raman spectrum of the as loaded GF sample exhibits a 2D/G ratio of ~1.7 and a D/G ratio of ~ 0.06 which indicate graphene of reasonable quality, the cycled samples show signs of degradation. In the spectrum of the three-times cycled samples the defect related D peak is clearly visible pointing to a larger portion of defects present in the graphene. This peak is no longer visible for the five times cycled sample. However, considering the very low intensities of the G and 2D peaks and the higher Cu oxide peaks this is not surprising. On the contrary, the graphene to Cu intensity proves a low graphene coverage due to the burning/etching of carbon during the T-R-cycling (see text for details).

Raman spectra of the MLG sample show similar quality.
SI Figure 2: a) SEM micrograph of five-times cycled Graphene flakes (GFb) according to table SI 1. The border line visible between the darker area in the upper and the brighter area in the lower part of the micrograph represents a Cu grain boundary. b) Corresponding local EDX taken in spots a (red) and b (black, dashed) of figure (b). c) Detail SEM micrograph of as loaded Graphene flakes. The white lines mark grain boundaries with overlapping graphene flakes. A bright spot is indicated by circle and arrow. d) EDX (HV = 5kV) taken in the bright spot of figure c).

The SEM micrographs are colored for better contrast. Darker areas comprise of graphene, light pink marks bare Cu and Si oxide particles are white, partially inked in blue.

Compared to the EDX spectra depicted in figure 1c) the oxygen contribution visible in the EDX spectrum of the graphene free Cu area in SI figure 1 is considerably higher. Apparently, larger bare Cu areas are more effectively oxidized than Cu underneath or in between closely packed GFs. The EDX spectrum of the bright spot in SI figure 1c) clearly indicates Si oxide. Note, that such spots are scarce and, according to the results of figure 1e) do not notably contribute to the total oxygen content of the samples.
SI Figure 3: a) Evolution of O1s spectra of three times cycled GFs (sample GFa, SI table 1) during the first of three cycles of heating and reoxidation recorded with two different photon energies representing surface and depth sensitive conditions (left: $E_{\text{kin}}$=150eV, right: $E_{\text{kin}}$=450eV). b) Evolution of relative intensities of the fitted components of the O1s region of all three cycles of sample GFa) normalized to the respective highest intensity in surface (top) and depth sensitive mode (bottom) during cycling. Arrows indicate the most defined 284.4eV (green) and 284.7eV peaks (black) in the corresponding C1s region. Fits in a) and b) were performed according to table 1.

Under low oxygen chemical potentials (i.e. in HV and UHV) copper metal is terminated by atomic oxygen, giving rise to various oxygen-reconstructed surfaces. The O1s spectra can be used to identify various oxygen species present on Cu and Cu$_2$O surfaces. Oxygen species of O-terminated metal surfaces such as O-Cu(110)-$[2\times1]$, O-Cu(110)-c$[6\times2]$, O-Cu(111)-“$44$”, O-Cu(111)-“$29$”, O-Cu(100)-c$[2\times2]$ and O-Cu(100)-$[2\sqrt{2}\times\sqrt{2}]R45^\circ$ appear within the range of 529.6-529.8 eV. While the reconstructions on the Cu(100) and Cu(110) surfaces are rather well ordered and smooth, the O-reconstructed Cu(111) surfaces are rather disordered and highly corrugated. It is interesting to note that the Cu$_2$O and the intercalated oxygen Cu surfaces both contain oxygen species at binding energies lower than that of the lattice oxygen of Cu$_2$O. This is likely a consequence of the lower coordination of these oxygen species.

Whereas the deconvolution in SI figures 3a) and b) required the same set of peaks for both photon energies, the ratio between Cu related and carbon-oxygen related peaks is clearly different. The higher intensities of the carbon-oxygen components with respect to the Cu related peaks in the surface sensitive spectra locate the former on the surface whereas the latter is rather located beneath the carbon layer. The trend shown in SI figure 3a) is retained throughout all three cycles as depicted in SI figure 2b).
SI Figure 4: a) Fitted C1s spectra recorded before and after oxygen intercalation and carbon etching/burning, respectively (from bottom to top; \( p_{O_2} = 0.2 \) mbar) corresponding to figure 4. b) Evolution of the relative abundance of the different carbon species of GF/Cu samples during heating in \( 5 \times 10^{-3} \), \( 5 \times 10^{-2} \) and 0.2 mbar oxygen as derived from fits of the respective C1s spectra according to table 1. Prior to the experiments shown here the intercalated oxygen of the initially long term air stored GF/Cu samples was removed by heating up to 600°C in vacuum. c) Top: Arrhenius plot of the graphene component at 284.75 eV derived from spectra recorded during de-intercalation by heating to 600°C. The sample was later exposed to 0.2 mbar of \( O_2 \) as described in figure 4. Bottom: Arrhenius plot of the oxygen component at 529.7 eV derived from spectra of cycle 1 in SI figure 3a) recorded during de-intercalation by heating to 600°C.

The fitted spectra presented in SI figure 4a) were taken at temperatures reflecting distinct changes of the C1s states during the intercalation experiment. As expected, at 200°C the spectrum is dominated by a 284.75 eV component representing a strong interaction of graphene with Cu. At 270°C the oxygen intercalation is complete as visible by the dominating 284.4 eV peak. The spectrum recorded at 380°C shows the last carbon intensities before the carbon is irrevocably etched away. Note, that the peak shapes are virtually the same as in the spectrum recorded at 250°C.

The relative abundance of peaks shown in SI figure 4b) demonstrate that the intercalation temperature window is largely independent of the oxygen pressure while graphene burning/etching clearly is dependent.

The determination of the intercalation activation energy in this work is based on the assumption of a linear correlation between the graphene coverage and intercalating oxygen. As explained in the main text, most of the involved fitted components are influenced by several overlapping processes, e.g. in the case of O1s spectra the formation of Cu oxides on bare Cu and underneath graphene covered areas. For this reason there is no O1s component solely affected by de- or intercalation whereas for the C1s region with the peak at 284.7 eV there is one component unaffected by other than de- and intercalation. Hence the latter peak is considered best to evaluate the de- and intercalation activation energies. To obtain at least a rough comparison between carbon and oxygen, the O1s component at 529.7 eV representing substochiometric Cu oxide was used as well. As discussed in the section “Aging by T-R-cycling and oxygen depth profiling” this component should represent mostly intercalated oxygen. SI figure 4c) shows the Arrhenius plots derived from C1s spectra during oxygen de-intercalation by heating to 600°C prior to oxygen exposure of the sample displayed in SI figure 4a) and from surface sensitive O1s spectra during oxygen de-intercalation of cycle 1 displayed in SI figure 3a. Note that the number of data points is limited to those higher temperatures because of contaminants due to air exposure at RT. The activation energies resulted in 0.18 eV for the C1s peak and 0.14 eV for the O1s peak which is good agreement and corroborates the assumption of a linear proportion of oxygen and carbon.
SI Figure 5: Evolution of Cu LMM (a) and O1s spectra (b) and (c)) of FLG during heating and cooling in vacuum. O1s spectra were recorded with two different photon energies representing surface and depth sensitive conditions. BE positions of Cu-oxygen and carbon oxygen bonds are indicated.
SI Figure 6: a) Work function determined during each preparation step of a three times cycled sample (see fig. 6 and SI table 1 for details). b) WF changes of a five time cycled sample during cycle 4 and 5 (see SI table 1 for details). Note: Arrows indicate the most defined 284.4eV (green) and 284.7eV C1s peaks (black)

Details about the evolution of the WF are given in the discussion of figure 6 of the main text.

SI Movie: ESEM movie of figure 3a).

References