Graphene oxide (GO) is described as a derivative of graphene obtained by oxidation of graphite or graphene.[1] The sp²-bonded carbon atoms, which are arranged in a honeycomb lattice, are partially decorated with oxygen-containing species.[2] Tuning the sp²/sp³ ratio in the GO materials provides pathways to design diverse graphene derivatives with intriguing physicochemical properties including surface modifiability,[3] tunable band gap,[4] and variable luminescence[5] for extensive applications in sensing based on electronic and luminescent devices.[6] However, because of the polydisperse structure of GO, the structural model remains generalized, in particular with respect to the regiochemistry.[6,7] During the preparation of GO via oxidation approaches such as Hummers’ method,[8] over-oxidation violently disintegrates the sp²-carbon lattice and results in either vacancy defects on the scale of 10 nm at best or flake-like amorphous carbon.[9] The size of defect-free graphene patches in reduced GO is about 1 nm.[10] Over-oxidation during the preparation of GO was identified as the reason for the ruptured graphene lattice in GO due to the loss of carbon via formation of CO₂.[11] As verified by Dimiev et al. using Hummers’ method in a first approximation, one CO₂ molecule is formed from 20 carbon atoms.[12] Recently, we found that kinetically controlled oxidation procedures can effectively hinder the over-oxidation, and the oxidation can still be performed by harsh oxidants such as potassium permanganate in sulfuric acid or sodium chlorate in nitric acid.[13] The obtained GO materials, which are a subclass of GO, are termed as oxo-functionalized graphene (oxo-G). The oxo-G bears an intact carbon framework with densities of lattice defects of about 0.02% and 0.5%.[14] It was demonstrated that hydroxyl, epoxy, and organosulfate groups decorate the carbon lattice on both sides of the basal plane and edge functional groups like carbonyl and carboxyl groups only play a minor role.[13]

The carbon lattice in oxo-G can be visualized by high-resolution transmission electron microscopy (TEM).[15] Chemically processed oxo-G with a degree of oxo-functionalization of about 4% (abbreviated as oxo-G₄%) bears defect-free areas with diameters of about 10 nm on average.[16] After thermal processing up to 175°C, the oxo-G₄% disproportionates and bears preserved graphene domains with diameters of about 3 nm, next to few-atom large vacancy defects and holes with diameters of around 1–2 nm.[16]

Oxo-G with a typical degree of functionalization of 60% (oxo-G₆₀%) displays a density of defects of about 2% after annealing.[16,17] Those defects can act as structural motifs and active sites for selective chemical functionalization.[17] So far, the vast majority of studies on GO or oxo-G based materials mainly focused on optimizing preparation and reduction methods,[15] understanding preparation protocols, probing the reduction mechanism,[18] and developing applications.[19] However, deep knowledge about the atomic structures and defects between oxidized and deoxygenated states in oxo-G are ambiguous. In particular, it is still not clear how the...
structure of GO or oxo-G_{60%} evolves during thermal processing.

Here, we present the structure evolution and related transport properties of oxo-G_{60%} on the single-layer level by gradual thermally induced disproportionation. The mobility values of monolayer oxo-G first increased with the release of adsorbed water, disproportionation up to 220°C and then decreased due to the formation of holes and surprisingly discovered stacked regions bearing sp^3-C. By X-ray photoelectron spectroscopy (XPS), we identified a fraction of about 26% C–C sp^3 and about 3.4% C–O/C–OH/C–O–C, containing nanometer-sized sp^3-patches as visualized by TEM. Those regions turned out to be semiconducting with a band gap of 0.4 eV, as revealed by scanning tunneling spectroscopy (STS). Thus, sp^2-C isolated by sp^3-patches is most likely responsible for the local semiconducting behavior (see Scheme 1 and Figure 5).

The starting oxo-G material used here possesses a degree of functionalization of about 60% sp^3-carbon, with hydroxyl, epoxy, and organosulfate groups as major functional groups.[21]

Temperature-dependent electrical transport properties were studied by fabricating and analyzing a monolayer oxo-G-based field-effect transistor (FET) device (Figure 1 A). The oxo-G device was fabricated by deposition of a monolayer oxo-G flakes on a heavily p-doped Si substrate with a 300 nm thick SiO_2 layer (Si/SiO_2) using the Langmuir–Blodgett technique.[22] Then, gold contacts were deposited on top of the monolayer oxo-G flake by standard electron beam lithography (EBL) and gold evaporation. All electrical transport measurements were carried out with a two-probe configuration (see Figure 1B) under ambient conditions. The Si/SiO_2 substrate serves as a back-gate and gate dielectric. Different transport performances were obtained by iteratively heating the same device with the same oxo-G flake from room temperature (RT) to 300°C. All transfer characteristics (I_{ds}-V_{bg}) reveal typical p-type behavior (Figure 1 C–J). The large hysteresis between forward and reverse sweeps is induced by trapped charges.[23] The resistance and charge carrier mobility are extracted from the transport curves in Figure 1 C–J. As depicted in Figure 1 K, on-resistance of oxo-G FET at V_{ds} = 0.5 V and V_{bg} = 0 V decreases from 5.3 × 10^6 Ω to 3.3 × 10^5 Ω. Evolution of the resistances reveals that the oxo-G undergoes an insulator to conductor transition with a partial restoration of sp^2-carbon lattices in the oxo-G flake by thermal processing. The change of hole mobilities (µ_h) displays an inverted parabola shape. The µ_h of the untreated monolayer oxo-G is 0.004 cm^2 V^1 s^1 is very low, as expected due to the insulating nature. After thermal annealing up to 100°C, the µ_h increases by an order of magnitude. This is
because most polar adsorbents like water or oxygen molecules desorbed from the oxo-G surface, as we identified before by thermogravimetric analysis.[31] In addition, some decomposition of organosulfate groups takes place.[24] But overall, the carbon skeleton of the oxo-G remains relatively intact until 100 °C.[25] Then, significant increase of the \( \mu_b \) is observed between 140 °C and 220 °C. It can be deduced that the main deoxidation process occurs at this stage, which is accompanied by formation of 7-conjugated domains, in addition to vacancy defects, small holes, and CO\(_2\), as evidenced for oxo-G\(_{300°C}\).[16] The maximum \( \mu_b \) of about 0.3 cm\(^2\) V\(^{-1}\) s\(^{-1}\) is obtained from oxo-G\(_{300°C}\), which indicates the maximized sp\(^3\) graphene structures in oxo-G\(_{300°C}\). In contrast, further annealing at higher temperature results in decreased \( \mu_b \) values. These results clearly suggest the limited restoration of the graphene domains and irreversible structural decay of oxo-G induced by the thermal processing.

Next, XPS was conducted to analyze changes in the chemical composition of an iteratively annealed oxo-G sample. The high-resolution C 1s spectrum of oxo-G in Figure 2A displays a typical saddle-like pattern, which stems from significant oxidation in oxo-G. Four components assigned to C\(_2\), C\(_{sp^3}\), C\(_{sp^2}\), and C\(_{sp^1}\) are deconvoluted. The initial C/O ratio of oxo-G was 2.2:1. No significant change of the COOH (2.5%, at 288.6 eV) are deconvoluted. The initial C/O ratio of oxo-G in the structural decay of oxo-G induced by the thermal processing.

To further prove the presence and impact of the sp\(^3\)-areas, we conducted scanning tunneling microscopy (STM) and spectroscopy (STS). With STS we surprisingly found local semiconductor properties. First, the morphology of the oxo-G\(_{300°C}\) was examined by STM. Figure 4A shows a large-scale STM image of a single oxo-G\(_{300°C}\) flake on highly oriented pyrolytic graphite (HOPG). The average height of the single layer is about 2.0 nm, which is almost twice the thickness of monolayer oxo-G, as we reported before.[28] This is ascribed to fluctuations of the carbon plane caused by the rearrangement and loss of monoatomic carbon in oxo-G after thermal annealing, as TEM showed. With increased magnification of

![Figure 2](https://www.angewandte.org/-content/13657-13662)

**Figure 2.** High-resolution C 1s XPS of oxo-G treated by iteratively annealing up to 300 °C.
the oxo-G$_{300}$C surface, dome-shaped morphologies were detected (Figure 4B). There are three differently colored distributions in Figure 4B: dark, brown, and bright. Height profiles in Figure 4C show the height difference from the bright plane to the brown plane, and from the dark plane to the brown plane of 0.9 and 1 nm, respectively. The topographical fluctuation over a 50 nm range is 1.9 nm, which nearly coincides with the thickness of this single layer. This indirectly indicates that the dark, brown, and bright regions correspond to holes, graphene domains, and stacked double-layer carbon, respectively.

The local electronic properties of these heterogeneous topographical surfaces in the oxo-G$_{300}$C sample were investigated via STS. The differential conductivity (dI/dV), which is proportional to the local density of states (LDOS) at small bias, was simultaneously obtained during the STM measurements using a grid I–V scan. The dI/dV curves in Figure S4 were obtained by averaging 3600 dI/dV curves recorded on the HOPG and the oxo-G$_{300}$C surface at respective places, respectively, as labeled in Figure 4B. The dI/dV spectrum of HOPG shows a nearly symmetrical parabolic geometry. The oxo-G$_{300}$C exhibits a V-shaped dI/dV reminiscent of two-dimensional Dirac material. The Dirac point is located at +40 mV. This p-type doping here is in agreement with the transport measurements in Figure 2J determined on micrometer-sized channels. The specific electronic information at different positions (marked as A, B, C, and D, shown in Figure 4B) was depicted by the local dI/dV spectra in Figure 4D (individual data shown in Figure S8). Obviously, the measured four positions present a distinct electrical inhomogeneity. First, the black line (measured at dark areas such as position A) shows a metallic-like behavior, similar to the LDOS behavior of HOPG,[29] which confirms that the dark areas are holes. Then, the red line (measured at brown areas like position B) shows a conical-shaped curve, corresponding to single-layer graphene structures.[30] It is worth noting that the fluctuations marked with the red arrow represent defective states, indicating some defects exist in the single-layer graphene structure. Two prominent peaks marked with blue arrows are observed in the blue line (measured at bright areas like position C). Similar STS spectra were also found in twisted graphene bilayers.[31] The two saddle peaks are attributed to energy separations of the low-energy van Hove singularities (VHSs) in graphene bilayers. Therefore, it can be demonstrated that the bright regions contain some sp$^2$-hybridized double-layer graphene structures. It is in particular interesting that a suppressed dI/dV distribution (green line) is measured at the brighter areas (position D, cf. Figure S8). The green averaged dI/dV curve (Figure 4D) represents typical semiconducting behavior[30,32] with a band gap of around 0.4 eV (Figure 4D). Combining the atomically resolved carbon structures (Figure 3 and Figure 4B) with the height of 1.9 nm (Figure 4C) at position D, we thereby deduce that such a large band gap can be attributed to formed conjugated sp$^2$-C, which is isolated from the surrounding graphene lattice.

As detected by XPS, the sp$^3$-sp$^3$-C and C–O/C–OH/C–O–C of 3.4 %, can act as insulators (illustrated in Figure 5). Their appearance might be related to the in-plane disruption of carbon–carbon bonds during the formation of holes, whereby the released carbon fragments react with the underlying graphene by sp$^3$-hybridization (Figure 5). Since the semiconducting areas make up 25 % (based on TEM area analysis) of the entire carbon layer, their effect on the overall band.
structure of oxo-G is almost insignificant. The formation of sp² carbon upon thermal disproportionation of oxo-G is supported by FTIR investigations in Figure S5, due to the IR-active signal at about 1570 cm⁻¹, a signal that was also found in nanodiamonds with sp³-patches. Moreover C–H bond cleavage may play a role, as evidenced by FTIR (2920 cm⁻¹ and 2850 cm⁻¹, Figure S5); however, elimination of water is more likely up to 140°C.

In summary, it can be stated that sp³-sp³ diamond-like, imperfect sp³-sp²-sp³, and C–O–C bridged out-of-plane structures open a new path to semiconducting graphene-based materials. Here, we describe the defect structures including holes and bilayer sp³-patches induced by thermal disproportion of the oxo-G. The identified C–C sp³-patches and bridging C–O–C motifs, which are connected to nm-sized patches of the hexagonal carbon lattice of graphene, are separated by grain boundaries and holes that are 5 nm in diameter. We suggest that C–C sp³-bonds are formed either after folding or adsorption of carbon patches, indicating that reactive species, including C–O structures, are formed in the course of the disproportionation reaction. The sp³-patches isolate residual sp²-C and thus local STS reveals the semiconducting behavior of these areas. It turns out that the nm-sized mixed sp²- and sp³-structures have a band gap of ≈0.4 eV. Our study indicates that semiconductor/graphene hybrid materials are interesting materials with local semiconducting properties. With this deeper insight into the thermal disproportionation of oxo-G and correlation to the electrical properties, future applications and the development of carbon-based semiconductors becomes possible. In particular, the formation of holes and sp³-stacked regions potentially plays a significant role for chemical reactions used to post-functionalize materials. Moreover, bottom-up synthesized molecular carbon materials containing sp³- and sp²-carbon with a tunable band-gap might be discovered in the future.

Acknowledgements

This research is supported by the China Scholarship Council (CSC), the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), project number 392444269. C.N. and A.T. acknowledge DFG financial support via the research infrastructure grant INST 275/257-1 FUGG (project no. 313713174).

Conflict of interest

The authors declare no conflict of interest.

Keywords: electrical transport properties · graphene oxide · microscopy · oxo-functionalized graphene · semiconductors

[7] See ref. [2b].

Figure S5. Schematic illustration of a proposed chemical structure of thermally processed oxo-G, accounting for mixed sp²- and sp³-C structures, which include ether-like connections and possibly carbonyl and hydroxyl groups at the rims. The idealized sp³-structures insulate conjugated sp²-channels, which are identified as semiconducting.


