# Photoinduced Reduction Mechanism of Graphene Oxide Revealed by Ultrafast Structural Dynamics

Graphene oxide (GO) exhibits broad applications because the atomic structure and physical properties of its reduced form resemble those of graphene and also because it is dispersible in water and functionalized by chemical methods. Understanding the reduction mechanisms of GO is important for controlling their properties. Herein, we employ ultrafast time-resolved electron diffraction and ultrafast mid-infrared vibrational spectroscopy to observe the reduction process. Our findings with theoretical calculations explain how and why the oxygen atoms of epoxy groups are selectively removed from the basal plane of GO by ultraviolet photoexcitation.

Graphene oxide (GO) is a derivative of graphene that is produced by chemical oxidation of graphite and offers a variety of applications. The high popularity of GO can be ascribed to the fact that the atomic framework and physical properties of its reduced form (rGO) are similar to those of graphene. Another reason is the high dispersibility of GO in water and polar organic solvents, where GO is easily functionalized by chemical methods. The dispersibility of GO in water is attributed to the presence of oxygenated functional groups such as hydroxyl, epoxy, carbonyl, and carboxyl groups. Notably, graphene has a flat structure featuring two-dimensionally spread six-membered carbon rings, whereas the presence of the above functional groups in GO and rGO results in the formation of quasi-two-dimensional non-uniform networks. The reduction of GO to rGO, accompanied by the partial removal of the oxygenated functional groups, can be easily achieved by exposing GO to reducing agents, high temperature, or ultraviolet (UV) light. However, the reduction mechanism of GO has not been fully clarified yet. Herein, we applied ultrafast electron diffraction measurements and ultrafast mid-infrared vibrational spectroscopy to GO upon UV-photoexcitation to directly observe its reduction process [1]. The obtained reduction mechanism from GO to rGO was compared with that determined by theoretical calculations.

**Figure 1a** shows the electron diffraction pattern obtained from the GO thin film, revealing the presence of six symmetrically arranged spots (corresponding to larger GO flakes) and several rings (ascribed to randomly oriented smaller GO flakes). **Figure 1b** shows the radial averaged data obtained for electron diffraction from GO thin film before and after exposure to UV-light (wavelength = 266 nm) with the diffraction rings of (100) and (110) planes. The average length of C–C bonds (1.431 Å) in the basal plane of GO calculated based on the positions of the above diffraction rings slightly exceeded that of graphene (1.417 Å) before perturbation, which undergoes contraction to the bond length of 1.417 Å after UV-light exposure above the fluence of 4 mJ/cm$^2$. Based on B3LYP/6-31G** level density functional theory (DFT) calculations and force field calculations on model graphene and GO structures, the lattice shrinkage of GO upon photoexcitation corresponds to the deoxygenation of epoxy groups in the basal plane of GO.

**Figure 1c** shows the evolution of the average C–C bond length in GO induced by photoexcitation with UV light as a function of time. The removal of the oxygen functional group from the basal plane of GO is not a reversible reaction. However, as the epoxy oxygen is connected to carbon atoms via two bonds, the reduction of epoxy groups requires the dissociation of two C–O bonds. Only one bond of an epoxy oxygen was broken by excitation with UV light at a lower fluence (2 mJ/cm$^2$), which realizes a reversible reaction. The photoinduced bond breaking and subsequent C–C bond shrinkage, namely, the processes of photoinduced reduction, occurred on a time scale of 40 ± 8 ps, which agrees well with the timescales (53 ± 3 and 42 ± 5 ps) of the time-dependent vibrational spectra around the epoxy group region (**Fig. 1d**) at wavenumbers of 1060 and 1100 cm$^{-1}$. Nonadiabatic quantum molecular dynamics based on time-dependent DFT calculations were performed on the graphene model with an epoxy oxygen to answer the question of why the epoxy groups were selectively dissociated from GO upon excitation with UV light. Electrons reside in the HOMO in the ground state, and an electron is eventually transported from the HOMO to the LUMO in the excited (or charge) state. The spatial distribution of the wave function for the C–O bonds of GO models with epoxy groups changes significantly before and after the excitation, and **Figs. 1e** and **1f** show the bonding (HOMO) and the antibonding (LUMO) characteristics, respectively.

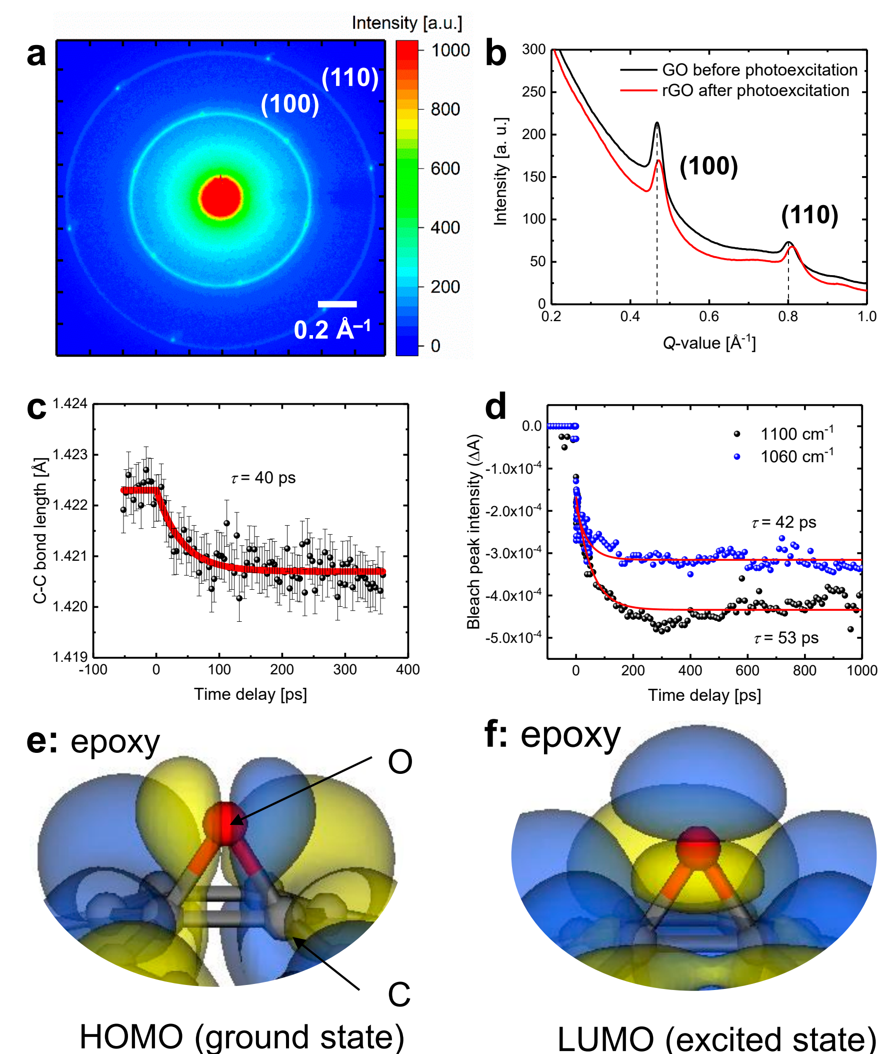


**Figure 1: a** Electron diffraction pattern from GO thin film and **b** the radial average of diffraction patterns before and after UV photoexcitation. Time-evolution of **c** C–C bond length obtained by ultrafast time-resolved electron diffraction and **d** the bleach peak intensity of ultrafast mid-infrared vibrational spectroscopy at wavenumbers of 1060 and 1100 cm$^{-1}$. **e**, **f** Spatial distribution of the wave functions of GO models with an epoxy oxygen in the HOMO and LUMO.

In summary, based on the experimental findings and the nonadiabatic calculations, we propose the reduction mechanism of GO as follows. The basal plane of GO possesses a graphene backbone and aperiodic defects, edges, and oxygen functional groups. Photoexcitation with UV light drives electrons from the valence band to the conduction band of the graphene parts in GO because the energy of UV light is equivalent to the $\pi$-plasmon band energy of graphene. The hot electrons in the $\pi$-plasmon band are delocalized on the basal plane of GO and transferred to the localized states in the LUMO of the epoxy groups (C–O–C). Due to the antibonding character of GO with epoxy groups, the potential energy required to remove the oxygen atoms in epoxy groups decreases in the charged or excited state. This electron transfer induces the selective removal of oxygen atoms in epoxy groups via photoexcitation on a timescale of 40–50 ps.

## REFERENCE

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## BEAMLINE

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