Transmission Electron Microscopy of Graphene: Stability and Dynamics of Ad-atoms and Ad-molecules

The functionality and in particular the electronic structure of graphene can be controlled by ad-atoms or ad-molecules that locally attach to the 2D graphene lattice. In the case of oxygen in the role of the adatom, the decorated material is a semiconductor referred to as graphene oxide whose properties are tunable by the degree of oxidation. Yet, for many other ad-atoms or ad-molecules the adhesion and migration energies are too small to warrant that the attached species is stable at room temperature.

Moreover, as the measurable physical properties, as, e.g., the mobility of the charge carriers, is lower than predicted by theory, it is suspected that local defects like for instance vacancies, ad-molecules or ad-atoms as well as topological defects account for this discrepancy. However, as the migration barriers of many ad-molecules and ad-atoms, which are likely present, are too small for forming stable local defects, it seems unlikely that they could be responsible for the reported discrepancy.

In contrast to the expected instability of ad-molecules, chromatic and spherical aberration-corrected atomic-resolution transmission electron microscopy (TEM) of small ad-molecules on graphene reveals that the molecules are stable at room temperature, and thus form stable (electronically active) defects. With the increased sensitivity of this novel imaging mode, it is possible to identify the site of the attached species on graphene, to qualitatively characterize their stability and to directly observe dynamics that takes place at the defect sites. On the basis of DFT calculations, atomic models are derived which can account for these observations. It is shown that TEM measurements and the DFT calculations provide evidence that ad-molecules and ad-atoms form symbiotic structures: ad-atoms and ad-molecules mutually trap each other on graphene. It is proposed to exploit the proposed atomic structures on graphene, in order to dope and functionalize graphene in a controlled manner.