# STABILITY AND DYNAMICS OF AD-ATOMS AND AD-MOLECULES ON GRAPHENE STUDIED BY ATOMIC RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

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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 ad-atom (see, e.g., [1]), 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. This, of course, makes it difficult to explain the effect of ad-atoms in a static picture.
Moreover, as the measurable physical properties, as, e.g., the mobility of the charge carriers, is lower than predicted by theory (see, e.g., [2]), it is suspected that local defects like such as 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 aberrationcorrected 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 defects that potentially are electronically active. With the increased sensitivity of this advanced TEM imaging mode, it is possible to identify the exact site of the attached species on graphene, to qualitatively characterize their stability and to directly observe dynamics that takes place at the defect sites under electron irradiation (see Figure 1). On the basis of density functional theory (DFT) calculations, atomic models and diffusion paths are derived which can explain the experimental TEM observations. It is shown that the 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,

explaining the unexpected stability of small ad-molecules on graphene.
Our finding that species attached to graphene find stable sites on adjacent carbon sites has two main consequences. Firstly, as ad-molecules can be trapped on graphene by the presence of ad-atoms, this mechanism could be exploited to dope and functionalize graphene in a controlled manner using a certain species of ad-molecules together with hydrogenated graphene.
Secondly, as functional groups find stable sites on graphene on positions next to each other, it seems likely that functionalizing of graphene occurs in patches, i.e. certain areas of graphene will be functionalized while others remain "clean". This can explain the experimentally observed structure of graphene oxide [1] where small patches of pristine graphene are surrounded by patches that contain a high density of oxygen functionalities (see Figure 2).

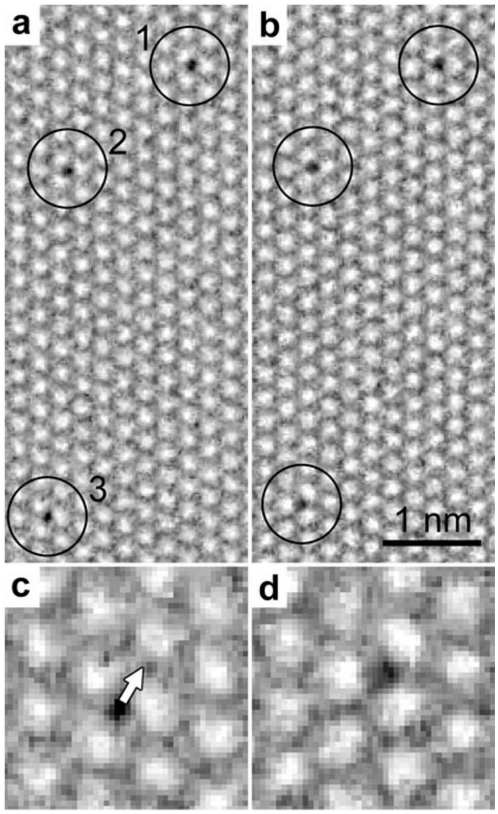


Figure 1: (a) Three ad-molecules are attached on a suspended graphene sheet (dark atoms). (b) Ad-molecule 3 moves from one $T$-site to another while being exposed to the 80 kV electron beam. (c) and (d) show details of (a) and (b).

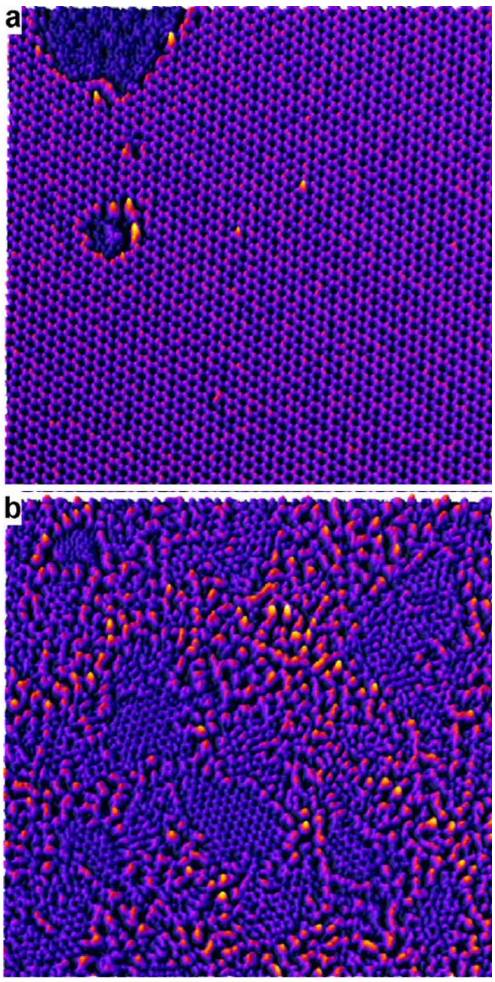


Figure 2: Phase images of reconstructed exit-plane waves showing in (a) the structure of graphene (including three ad-molecules and two holes) and in (b) the structure of graphene oxide which consists of patches of pristine graphene surrounded by areas of high oxygen functionalities.

## References

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