



Fig. 1 (a-f): Charge distribution, projected potentials and TEM simulations for nitrogen-doped graphene. (a) The relaxed atomic configuration for a nitrogen impurity substitution in graphene. Bond lengths are given in angstroms. (b) Projected potential based on the IAM (independent atom model). (c) TEM simulation based on the IAM potential, for two different defocus parameters  $f_1$  and  $f_2$ . Filters are: (i) unfiltered, (ii) periodic components removed, (iii) low-pass filtered. (d) Atomic structure with the changes in the projected electron density due to bonding shown in colour. (e) Projected potential based on the all-electron DFT calculation. (f) TEM simulations using the DFT-based potentials. The grey-scale calibration bar applies to columns (ii) and (iii), which are all shown on the same grey-scale range for direct comparison.

## Dresselhaus group comments

„Charges under the microscope“

March 2012 - Dresselhaus group comments that „An interesting application also involving AC-HRTEM is presented by Meyer et al. [1]. They demonstrate an experimental analysis of charge redistribution due to chemical bonding in nitrogen-doped graphene membranes and boron-nitride monolayers. Namely, the electronic charge density distribution of a solid contains information about the atomic structure and also about the electronic properties, such as the nature of the chemical bonds or the degree of ionization of atoms. This work turns out to be important because the redistribution of charge due to chemical bonding is small compared with the total charge density and is difficult to measure. Although the differences are small, a full understanding of how this charge redistribution works is needed. In other words, the electron scattering by a carbon atom next to a nitrogen atom turns out to be significantly different from electron scattering by a carbon atom elsewhere in the graphene sheet.

The success of Meyer et al. relies on AC-HRTEM measurements of defective sites in graphene. In this way, they correct the spherical aberrations of the microscope and do a defocus large enough so that in the contrast transfer function (CTF), features from the nitrogen can be distinguished from the carbon atoms. In order to explain the experiment they use first principles modeling techniques, considering the charge redistribution everywhere the nitrogen atom is located. In this context, they also show that the traditional independent atom model (IAM) analysis is inappropriate to properly interpret HRTEM results in defective samples. Fig. 1 above shows a comparison between the two methods of analysis and their consequences on the simulated HRTEM

images. Note that in Fig. 1 (c) it is seen that, no matter what is the defocus status, if one uses the IAM, the nitrogen atom cannot be distinguished. However, in Fig. (f), especially for the defocus status  $f_2$ , it is possible to clearly observe the effects of the hydrogen atom in the graphene lattice.

With this combination of techniques, the authors analyzed the charge transfer on the single-atom level for nitrogen-substitution point defects in graphene, and they confirm the ionicity of single-layer hexagonal boron nitride. Moreover, it is possible to obtain insights into the charge distribution in general nanoscale samples and non-periodic defects can be clearly observed in HRTEM measurements. They have shown that HRTEM experiments when used with first-principles electronic structure calculations opens a new way to investigate electronic configurations of point defects and other non-periodic arrangements of nanoscale objects that cannot be studied by a conventional electron or x-ray diffraction analysis. Moreover, this approach is also very promising for studying vacancy cluster defects, since the existence of vacancies will also require a local redistribution of charge densities.“

More information: Paulo T. Araujo, Mauricio Terrones, Mildred S. Dresselhaus. Defects and impurities in graphene-like materials, *Materials Today*, Volume 15, Issue 3, March 2012, Pages 98–109

Original publication: [1] J.C. Meyer et al. *Nature Materials*, 10 (2011), p. 209