First-principles study of nitrogen-doped and defective graphene

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Since the discovery of graphene, many efforts have been made to tailor this 2D material of a Dirac-cone bandgap structure without disturbing the high electron mobility.[1] However, fundamental understanding of the potential and the effect of doping and defect is still lacking. Here we present a systematic study of nitrogen doping on defective graphenes based on Density Functional Theory (DFT). Up to 6 adjacent carbon vacancies (V_C), nitrogen dopants (N_C), and defect complexes (nV_C+mN_C) were considered. In both pure vacancy defects and vacancy-doping complex scenarios, the geometries undergo a Jahn-Teller like distortion driven by the unterminated dangling bonds on carbon atoms. The pure nitrogen substitution defects have the lowest formation energy, particularly with one nitrogen substitution. When a vacancy defect exists, the nitrogen atoms prefer to substitute the positions around the vacancy. These defect complexes also have significant effect on its own electronic properties. In the $2V_C+4N_C$ defect configuration, the bandgap can be opened to 0.25 eV. The Fermi velocity of this defective graphene is 0.48×10^{-6} m/s, comparable to pristine graphene. Such insight is very important for the design of electronic devices, graphene-based catalysts and energy storage materials.

Reference:

[1] X. Wang, et al. "N-Doping of Graphene Through Electrothermal Reactions with Ammonia" *Science* **324** (2009): 768-771.

Figures:

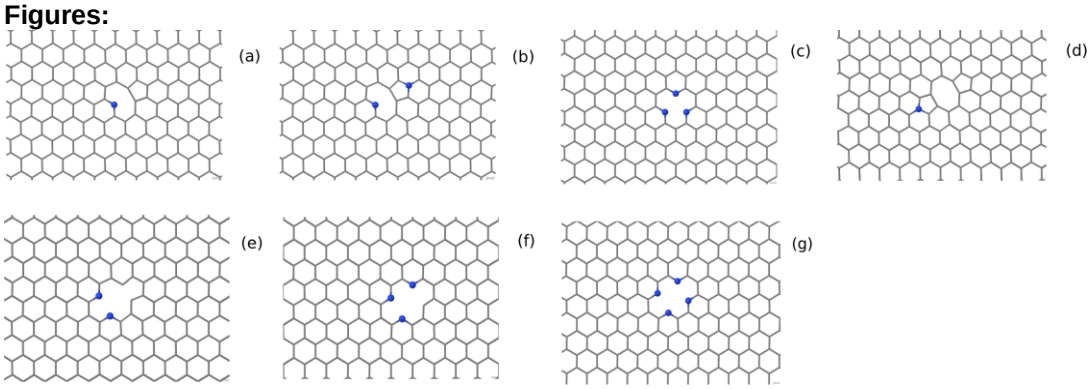

Figure 1: The nV_C+mN_C complex defective graphene configurations. (Blue atoms are nitrogen, and graphene is the grey framework.)

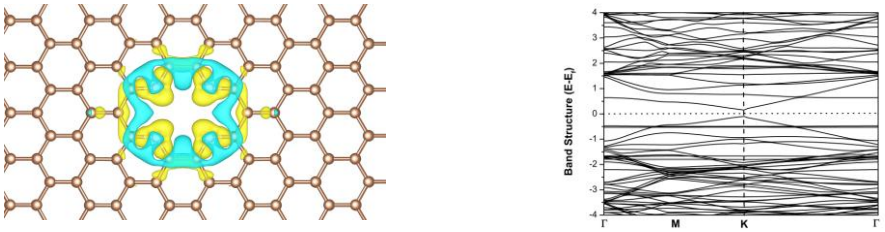

Figure 2: The charge difference of the $2V_C+4N_C$ defective graphene on the left (yellow represents the charge accumulated and blue is decreased area. Isosurface is set to 0.002 a_0^{-3}, where a_0 is the Bohr radius) and its band structure is shown on the right.