
THE EFFECT OF ATOMIC-SCALE DEFECTS AND DOPANTS ON GRAPHENE ELECTRONIC STRUCTURE

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Graphene, thanks to its extraordinary electronic and mechanical properties, is a potential candidate for a number of applications. Being one-atom thick, it is extremely sensitive to the presence of adsorbed atoms and molecules (either physisorbed or chemisorbed on the surface) and, more generally, to defects such as vacancies, holes and/or substitutional dopants. This property, apart from being directly usable, *e.g.*, in molecular sensor devices, can also be employed to tune graphene electronic properties.

In this contribution we review that basic features of atomic-scale defects that can be useful for material design[1]. We first focus on isolated "p_z defects" such as atom vacancies or simple adsorbed species covalently bound to carbon atoms, and on the effect they have on graphene electronic structure at the Fermi level through the formation of quasi-localized *midgap states* [2,3]. These states support an itinerant π electron picture which is usually invoked in π -conjugated hydrocarbon chemistry to explain the increased reactivity at specific lattice positions (see Fig.1). Therefore, when considering multiple defective structures, we need to take into account the possible effects such states have on sequential defects formation. This is the case, for instance, of adsorption of atomic species which typically occurs under strict *kinetic control* because of the presence of an energy barrier to sticking. In this context, we show why chemisorption of H atoms *cannot* occur randomly on the surface, and how *preferential sticking* mechanisms concur in forming *clusters* of adsorbed species [4,5].

Next we consider the reverse problem, that is how to engineer graphene electronic properties by arranging defects to form well-ordered structures, *e.g.* superlattices of nm-sized holes (see *e.g.* Ref. [6]). With the help of group theoretical arguments and electronic structure calculations, we show how it is possible to open a band-gap in graphene electronic structure *without* breaking its symmetry [7], namely by superimposing a *honeycomb* superstructure of defects to the honeycomb structure of graphene (Fig.2). The induced-gaps are comparable in size to those found in nanoribbons at the same length scale and, interestingly, come with novel Dirac cones right close to the gapped region. Similarly, we consider analogous superlattices of N and B substitutional dopants which show either a modified conical or a gapped quasi-conical structure, depending solely on the symmetry of the superlattice [8]. All these possible structures might find important technological applications in the development of novel graphene-based logic transistors, if progress in bottom-up techniques will make atomically- precise-fabrication possible in the near future.

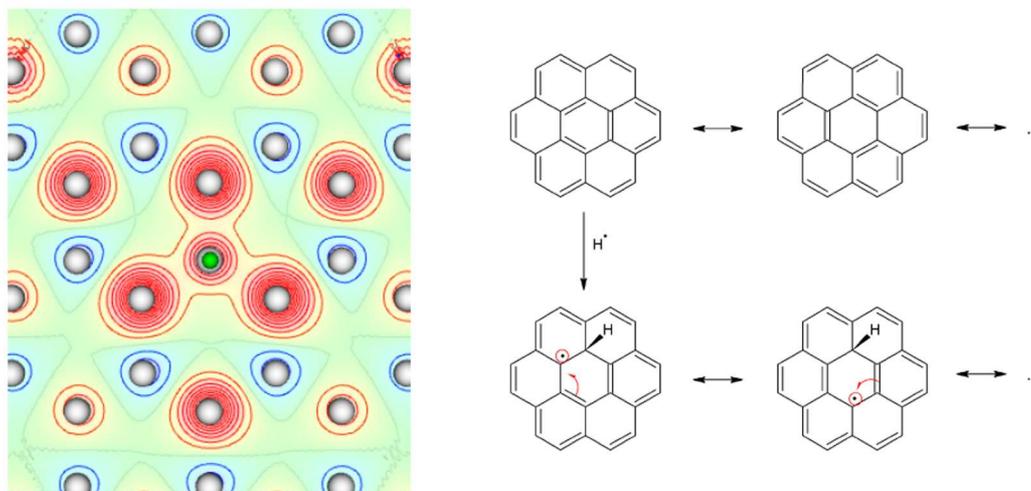


Figure 1: **Left:** The non-vanishing spin-density arising from the single occupation of the midgap state formed upon adsorption of a H atom (green ball). **Right:** the itinerant π -electron picture consistent with the spindensity shown on the left panel. The lattice positions where the spin-density localizes (red) have increased reactivity towards further hydrogenation.

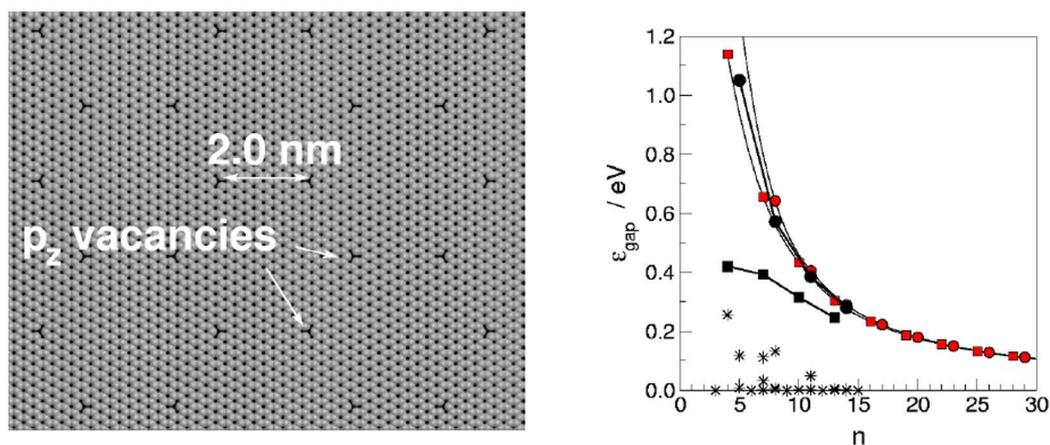


Figure 2: **Left:** A simple honeycomb superlattice of defects showing a symmetry-induced band-gap opening. The p_z vacancies may be either C atom vacancies or chemisorbed species. **Right:** band-gap size *vs.* superlattice constant n ($n=14$ in the left panel) for "defect dimers" arranged in honeycomb superstructures as computed at the tight-binding (red) and DFT (black) level of theory. In the latter case defects have been realized with H atoms. Crosses represent asymmetric arrangement of dimers in the same supercells.

References

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