Is nitrogen the key to obtaining codoped graphene?

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Abstract

To expand the range of applicability of graphene, the simultaneous introduction of two dopants may pave the way toward new two-dimensional materials with unique properties. The most important codoped graphene systems synthesized are: B/N, N/O, N/F, S/N, P/N, P/B, P/O, S/P, S/B. Si/N Cl/N Se/N, TMN (where TM is a metal), Fe/S, and Al/Ni [1-4]. From this list of codoped systems, it is crystal clear that nitrogen dominates the list. Therefore, the question emerges: are we co-doping graphene or doping N-doped graphene? The strong electron-withdrawing properties of nitrogen and its ability to form multiple bonds are crucial for introducing other heteroatoms. Also, nitrogen can be present in various forms, pyridinic, graphitic, and pyrrolic, that can adapt to the needs of the dopant. For example, in B/N doped graphene, it may prefer to be in graphitic form rather than pair boron. However, for S/N codoped graphene, it can adopt a pyridinic structure, allowing sulfur to be present in thiophenic form CSC. In the case of transition metals, they can be trapped in an N4 environment, as in porphyrins, anchoring the metal to the graphene's surface and avoiding the undesired metal clustering. By means of first-principles calculations, we analyze these with detail systems, explaining why nitrogen stabilizes the codoped systems and also demonstrating that, in most cases, the dopants prefer to be agglomerated instead of replacing random carbon atoms.

References

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Figures

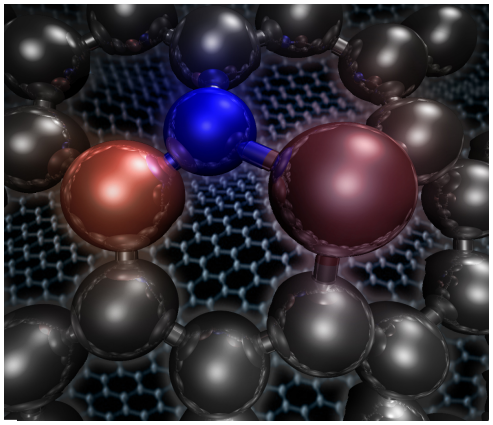

Figure 1: Theoretical calculations suggest that in most cases dopants in graphene prefer to be agglomerated, i.e. two dopants prefer to replace a CC bond instead of being separated. The most stable codoped graphene systems are obtained when one of the dopants is nitrogen.