2D $B_xC_yN_z$ layers as predicted by the cluster-expansion approach

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Graphene provided the excitement and impact to explore isolated one-atom thick layers that go beyond graphene. The boron-carbon-nitrogen 2D layers are now widely explored, since they exhibit a variety of structural and electronic properties that depend on the composition [1] and can lead to new functionalities. In this work, we develop strategies for predicting the most stable 2D $B_xC_yN_z$ layers. The idea is to find 2D materials that preserve the honeycomb-like structure and can complement graphene in properties. The modeling of these structures is done using the cluster-expansion method combined with extensive first-principles calculations.

Doping of graphene with carbon and boron atoms was studied before, using both first-principles [2, 3] and cluster-expansion [3] methods. The purpose of those studies was mainly to investigate the induced by doping band-gap opening in graphene. For instance, for the $C_{x-1}N_x$ system two stable ordered semiconducting structures, $C_{12}N$ and C_3N (x = 0.08 and 0.25, respectively), have been predicted through the cluster-expansion technique ($C_{12}N$ has a direct band gap of ~1 eV) [3]. In this work, we explore systematically the stability and properties of 2D $B_xC_yN_z$ layers with a full spectrum of compositions. For the mentioned above $C_{x-1}N_x$ system, we predict, for instance, that the most stable layer is obtained for x = 0.66. This is shown in Fig. 1 (right), where we plot the formation energy versus composition for various structures resulting from mixing C and N atoms. In this figure (to the left), we show the predicted structure by the cluster-expansion technique and the same structure after structural relaxation. Interestingly enough, our calculations reveal that the 2D layer splits into 1D stripes. The nanoribbons are only very loosely connected with each other (the stripes do not form mutual covalent bonds) and have a band gap of 2.9 eV. Furthermore, the building block of each nanoribbon is a C_2N_4 molecule (shown in the inset) with a 1.1 eV/molecule energy gain upon formation of the stripe.

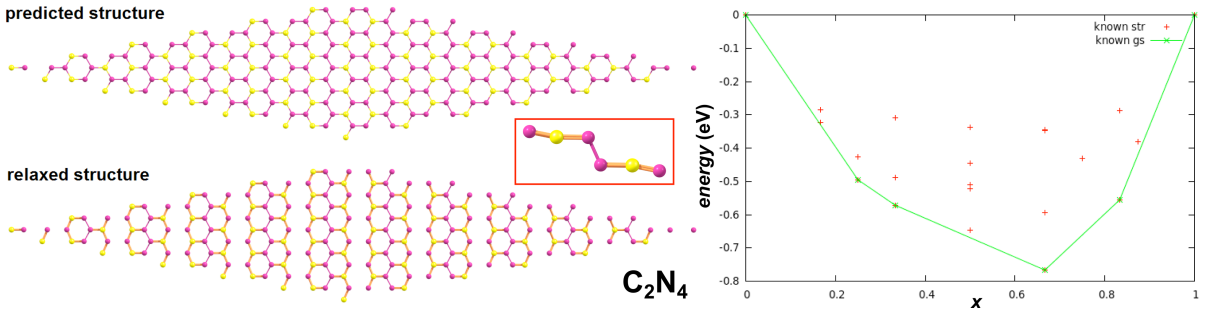

Fig. 1 The most stable 2D structure of C_2N_4 (left) and convex hull of the carbon-nitrogen system with the honeycomb structure (right). The formation energies are calculated with respect to graphene and the two-dimensional honeycomb nitrogen structure. It can be seen that C_2N_4 (x = 0.66) is the most stable structure among 2D $C_{x-1}N_x$ compounds. In the inset, we show the structure of the C_2N_4 molecule (azodicarbonitrile).

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