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Edge reconstructions of hexagonal boron nitride nanoribbons: A first-principles study

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HIGHLIGHTS

- The armchair BNNR is the most stable edge structure, followed by the ac-48 edge.
- The zigzag-like ac-56 edge is more stable than the pristine zigzag structures.
- ac-677 and ac-678 type reconstructions are suggested as possible edges in BNNR.
- The zz-57 reconstruction in hetero-elemental BNNR is different from that in GNR.

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ABSTRACT

The edge reconstructions of hexagonal boron nitride nanoribbons (BNNRs) and their stabilities have been investigated by the first-principles calculations of both their binding and edge energies. It is found from our calculations that the binding energy we have used is a reliable and useful quantity for judging the stabilities of different edge reconstructions of the hetero-elemental BNNRs instead of the conventional edge energy one, especially for those BNNR's edges with unequal number of B and N atoms. In addition, other four main results have been obtained: (1) the armchair BNNR is the most stable edge structure and the characteristic ac-48 edge reconstruction for the BNNRs is predicted to be the second most stable edge in all the discussed BNNR edge structures. But, its zigzag edge is less stable. (2) The zigzag-like ac-56 type reconstructions are more stable than the pristine zigzag structures, which is different from that of the graphene nanoribbon (GNR), being less stable than the zigzag GNR. (3) The stabilities of BNNR's ac-677 and ac-678 type edge reconstructions lie between its ac-56-B and zz-57-B edges. (4) The zz-57-B(-N) edge reconstruction lowers the edge energy by a small quantity, which is also different from that of GNR. Moreover, the zz-57-B edge structure is more stable than the zz-57-N one, indicating that B-rich edge is easier to be reconstructed while the N-rich edge is more stable. Our theoretical calculations suggest the many possible reconstructed edge structures for the bare BNNRs, which is important for BNNR's application in future nanoelectronics and spintronics.

1. Introduction

The two-dimensional (2D) nanosheets, such as graphene [1,2] and hexagonal boron-nitride (h-BN) [3,4], as well as their corresponding quasi-one-dimensional nanoribbons [5,6] have been intensively investigated in recent decades due to the distinctive physical properties, unfound in their bulk counterpart. A single h-BN layer has a honeycomb geometric structure, similar to that of graphene. But, there are different physical properties between both of them, e.g., the graphene is a semimetal with a zero band gap, while the h-BN sheet is a semiconductor with a wide direct band gap.

The graphene and h-BN nanoribbons can be obtained by cutting a finite-width slice from their infinite 2D sheets, both of which exhibit dramatic dependence of their electronic structures on the crystallographic orientation and termination of the edges [7–10]. For instance, the first-principles calculations confirm that for both the bare GNRs and BNNRs, all the armchair edge nanoribbons are semiconductors, while the zigzag edge ones are metals when the spin polarization is not included [8,9]. Besides, their magnetism strongly depends on their edge shapes, which only exists in their zigzag edge structures, while the armchair-edge ones are nonmagnetic [11,12].

Since the precise atomic geometry of the nanoribbon edge is expected to play a significant role in ribbon's physical and chemical properties, it is important to study the different possible edge structures and stabilities of the graphene and h-BN nanoribbons.

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The self-passivating edge reconstructions of the graphene nanoribbons (GNRs) have been predicted theoretically [13] and observed experimentally [14,15], which could happen for the pristine GNRs with dangling bonds by introducing the pentagons or heptagons into their edges, producing various edge structures, such as the zz-57, ac-677 and ac-56 edges in addition to two well-known zigzag and armchair edges. In all the different GNR edges, the zigzag edge is proved to be metastable, evolving easily into the zz-57 edge, which lowers the edge energy by a large value of 0.35 eV/Å and thus makes the zz-57 edge to have the lowest edge energy. The ac-677 edge energy is only slightly higher than that of the armchair edge, but still lower than that of the zigzag edge. The reconstructed ac-56 edge has the highest edge energy.

Therefore, it is naturally expected that the pristine BNNR's edges may also be unstable, causing thus their reconstructions, which is similar to those of the pristine GNRs. Mukherjee et al. have studied the stabilities of the armchair, zigzag and the reconstructed zz-57 edges of the BNNRs [16]. They found that the pristine armchair edges of BNNRs are the most stable, while the pristine zigzag edges of them are metastable, which favor the planar reconstructions by producing 5–7 rings for minimizing the edge energy. Wu et al. have also reported that the unpassivated nitrogen (N) edge of the zigzag edge BNNR is energetically less stable than the corresponding reconstructed one [17]. Besides, it has been reported that the h-BN flakes grown on Ni(111) are nitrogen-terminated triangles [18,19], which have lower edge energies than those of the boron-terminated ones [20]. Despite of all these studies, however, there are still no systematic studies on the more possible edge reconstructions and corresponding stabilities of the BNNRs at present.

In this paper, we have studied 14 different edges of bare BNNRs and their stabilities by using the first-principles calculations. It is found by comparing their binding and edge energies that the stabilities of these BNNR edges are different from those of the similar GNRs because the BNNR is the hetero-elemental system, in which the emergence of homo-elemental bonds on the edges will increase its edge energy.

The remainder of this paper is organized as follows. In Section 2, the geometrical structure and computational details are described. In Section 3, the main numerical results and some discussions are given. Finally, in Section 4, a conclusion is presented.

2. Model and method

BNNR's edges discussed in this work are all naked, i.e., without the hydrogen-termination. Their optimized geometric structures are shown in Fig. 1, in which the edge reconstruction is supposed to happen only at one edge of the BNNR; while the other edge

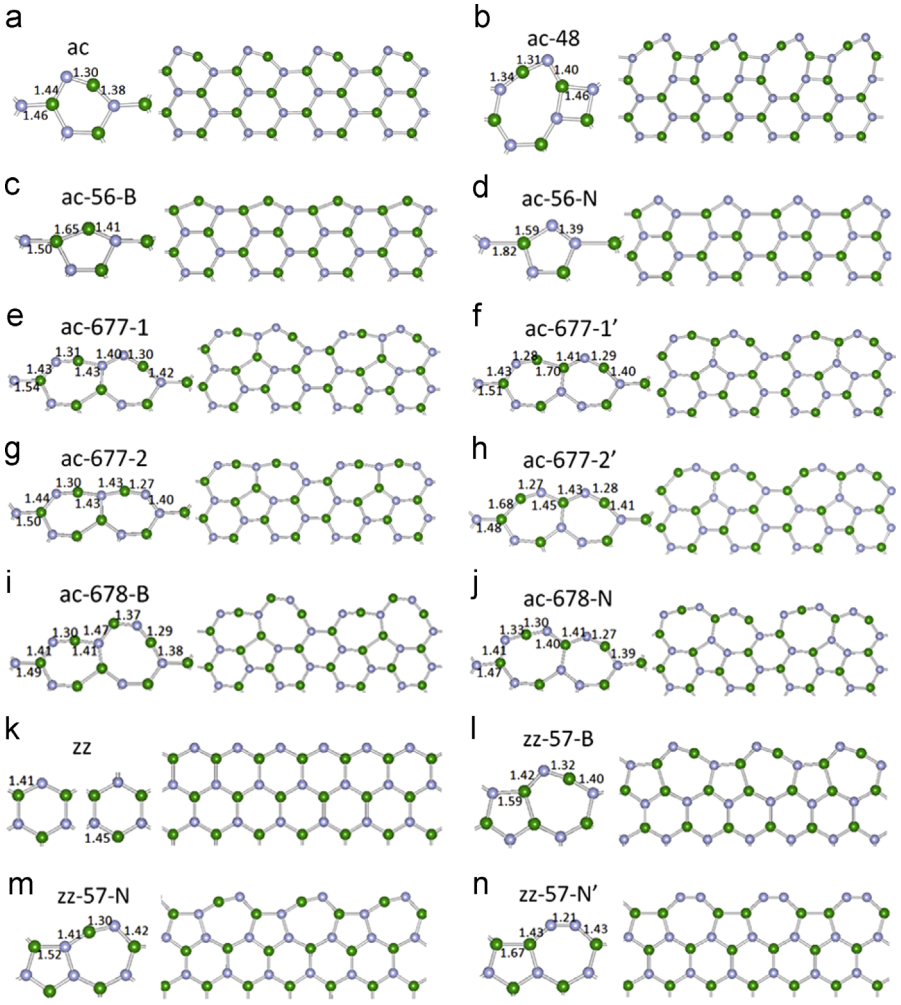

Fig. 1. The optimized geometrical structures of (a) armchair (ac), (b) ac-48, (c) ac-56-B, (d) ac-56-N, (e) ac-677-1, (f) ac-677-1′, (g) ac-677-2, (h) ac-677-2′, (i) ac-678-B, (j) ac-678-N, (k) zigzag (zz), (l) zz-57-B, (m) zz-57-N, and (n) zz-57-N′ BNNRs. Some bond lengths are shown on the left of each structure. The B and N atoms are represented by green and gray balls, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)