Nano-Stitching of Graphene Bilayers: A First-Principles Study

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A nano-stitching method is proposed and investigated to modify graphene bilayers. Based on this method, four types of low energy carbon allotropes, "wormhole graphene" allotropes, are obtained and their structures, stabilities and electronic properties are investigated using first principles methods. We find that all of these wormhole graphene allotropes are more favorable than graphdiyne and dynamically stable. Similar to carbon nanotubes and fullerenes, these graphene allotropes are expected to act as two-dimensional periodic nano-capsules for encapsulating magnetic atoms or functional clusters for a variety of applications.

Graphene [1, 2] is a single layer of carbon atoms in two-dimensional hexagonal lattice. It has attracted tremendous attentions owing to its peculiar electronic structures [2–5] since it was synthesized in 2004 [1, 2]. In the past decade, graphene layer has always been considered as nano-fabrics and geometrically cut into multifarious patterns [6–8] for the purposes of designing special functional segments using in integrated circuit. Electronic and magnetic properties of graphene can be efficiently modulated by such a geometrical cutting method [6–8]. For example, graphene nanoribbons with zigzag and armchair edge shapes show different electronic and magnetic properties [6]. Graphene layer has also been considered as nano-paper and chemically painted in different patterns with different functional atoms and/or molecules [9–11]. For example, a new type of 2D material graphene was theoretically proposed [12–18] and experimentally synthesized through exposing graphene to cold hydrogen plasma [10, 11]. These two main types of modification methods provide us efficient modulating effects on the physical properties of graphene.

In fact, graphene layer has also been considered as the building blocks to form carbon nanotubes, fullerenes and graphite. In this work, we theoretically propose a nano-stitching method to modify graphene bilayers for designing a new type of carbon-based material, which we named it as "wormhole graphene". Four stitching manners of graphene bilayers are considered and investigated, which have perfect interlayer links, C1 vacancy based interlayer links, C4 vacancy based interlayer links and C6 vacancy based interlayer links, respectively. Based on the 4x4 supercells of AA stacked graphene bilayer, four corresponding wormhole graphene allotropes are obtained and their structures, stabilities and electronic properties are investigated. We find that all of these wormhole graphene allotropes are more favorable than graphdiyne and dynamically stable. Similar to carbon nanotubes and fullerenes, these graphene allotropes are expected to act as 2D periodic nano-capsules for encapsulating magnetic atoms or clusters for different applications.

**COMPUTATIONAL DETAILS**

The nano-stitching method is schematically shown in Fig.1. The wormhole-like graphenes can be obtained through three steps: I). Stack two graphene layers in an AA-stacking manner with or without intercalated atoms/functional-clusters. II) Periodically etch the graphene bilayer into a bilayer nano-mesh with holes in different sizes, creating active dangling atoms at the edge of the holes. III). Compress the graphene bilayer nano-mesh to induce a reconstruction of the dangling atoms in different layers, "stitching" the two graphene layers together to form the wormhole graphene. Such a nano-stitching method can also be applied to h-BN bilayer and graphene/h-BN bilayer with or without intercalated functional atoms or clusters. In this work, we use the graphene bilayer without intercalated atoms/clusters to demonstrate the nano-stitching technology. Four types of stitching manners between graphene layers are considered and investigated, which have perfect interlayer links (P-IL), C1 vacancy based interlayer links (C1-IL), C4 vacancy based interlayer links (C4-IL) and C6 vacancy based interlayer links (C6-IL), as shown in Fig.2. Based on the 4x4 supercells of AA stacked graphene bilayer, four corresponding wormhole graphene allotropes are obtained and their structures, stabilities and electronic properties are investigated.

Our calculations were carried out using density functional theory with local density approximation [19, 20] (LDA) as implemented in Vienna ab initio simulation package (VASP) [21, 22]. The interactions between the nucleus and valence electrons of carbon atoms were described by the projector augmented wave (PAW) method.
RESULTS AND DISCUSSIONS

We first discuss the structural properties of these wormhole graphene allotropes. All the interlink junctions between graphene bilayers are constructed to be all-sp² configurations. After full optimization, the configurations maintain the all-sp². One can reproduce the crystal structures of the wormhole graphene allotropes based on their crystalline information as discussed below and see the details about the interlink junctions in any 3D view software. Crystal structure of P-IL belongs to the space group 162 (P-3M1) and possesses lattice constants of \(a=b=9.87 \, \text{Å}\) and \(c=18 \, \text{Å}\). It contains 64 carbon atoms in its crystal cell but only six of them are nonequivalent. The six nonequivalent atomic positions are \((0.848, 0.769, 0.536), (0.819, 0.652, 0.589), (0.661, 0.576, 0.611), (0.915, 0.585, 0.602), (0.578, 0.411, 0.617)\) and \((0.667, 0.333, 0.618)\), respectively. In P-IL, the interlayer chemical bonds are formed by 12 junction atoms from different layers. A -6-8-6-8 carbon rings sequence can be noticed in the junction area. C1-IL possesses the P-6M2 (187) symmetry and its lattice constants are \(a=b=9.732 \, \text{Å}\) and \(c=18 \, \text{Å}\). It contains 62 carbon atoms per crystal cell but most of them are equivalent. There are nine nonequivalent atomic positions in C1-IL. They are \((0.897, 0.794, 0.539), (0.747, 0.746, 0.577), (0.667, 0.834, 0.581), (0.501, 0.706, 0.596), (0.416, 0.583, 0.599), (0.499, 0.500, 0.603), (0.667, 0.584, 0.599), (0.750, 0.500, 0.603)\) and \((0.667, 0.333, 0.606)\). The interlayer bonds in C1-IL are formed by 6 junction atoms from different layers, forming a -10-10-10- carbon rings sequence. C4-IL possesses the P-6M2 (187) symmetry and its lattice constants are \(a=b=9.713 \, \text{Å}\) and \(c=18 \, \text{Å}\). The crystal cell of C4-IL contains 56 carbon atoms distributed in eight nonequivalent atomic positions. The eight nonequivalent positions are \((0.707, 0.729, 0.541), (0.654, 0.827, 0.573), (0.502, 0.751, 0.611), (0.517, 0.835, 0.611), (0.501, 0.001, 0.597), (0.418, 0.082, 0.578), (0.751, 0.249, 0.578)\) and \((0.667, 0.333, 0.587)\). The 12 junction atoms around the C4 vacancy bond to each other to form the junction with a -6-10-6-10-6-10- carbon rings sequence. For C6-IL, there are 52 carbon atoms in its hexagonal cell with lattice constants of C6-IL are \(a=b=9.782 \, \text{Å}\) and \(c=18 \, \text{Å}\). It belongs to the P6/MMM (191) space group and possesses only four nonequivalent carbon atoms locating at \((0.817, 0.635, 0.538), (0.665, 0.584, 0.575), (0.417, 0.583, 0.587)\) and \((0.667, 0.333, 0.586)\). In C6-IL, the interlayer junction with a -8-8-8- carbon rings sequence is formed by 12 carbon atoms from different layers.

The relative thermodynamic stabilities of these wormhole graphene allotropes were evaluated through comparing their average energies to those of graphene, T-graphene and graphdiyne. As shown in Fig.2, we can see that C1-IL is the most stable one among these four types of stitching manners. Although all of total energies of these wormhole graphene allotropes are higher than that of graphene, all of them are more favorable than the theoretically proposed T-graphene and the experimentally synthesized graphdiyne. Dynamical stabilities of these wormhole graphenes were also evaluated through calculating their vibrational properties. As shown in Fig.3, we plot the calculated phonon density of states of the wormhole graphene with P-IL, C1-IL, C4-IL and C6-IL interlinks, respectively.
We can see that there are not any vibrational modes in the imaginary frequency area in the whole Brillouin Zone, which confirms that all these wormhole graphene allotropes are dynamically stable. In view of the fact that graphdiyne has been experimentally synthesized, we expect these energetically more viable wormhole graphene allotropes can also be synthesized in the future through the nano-stitching method as discussed above.

After the discussion about the structures and stabilities of the wormhole graphene, we turn our attention to the electronic properties of these new carbon allotropes. The calculated electronic band structures of the four wormhole graphene allotropes are shown in Fig. 4. The band structure of a 4x4 AA-stacked bilayer graphene is also inserted for comparison. We can see that the P-IL possesses dirac-like property similar to that of the AA-stacked bilayer graphene around Fermi-level. But the band branches far from the Fermi-level are very different in P-IL and AA-stacked bilayer graphene, which indicates that interlayer bonds have strong modulation effects on the electronic properties. Furthermore, the dirac-cone in P-IL is located a little below the Fermi-level, which indicates that the interlayer bonding roles as n-type doping. The band structure of C1-IL shows obvious difference in comparison to that of the perfect AA-stacked bilayer graphene. The appearance of C1 vacancy and the interlayer bonding between vacancy atoms induce obvious p-type doping effect in the band structure, which moves the dirac-cone a little above the Fermi-level and makes C1-IL show metallic property. From the band structures we can see that such a p-type doping effect is more obvious in C4-IL and C6-IL. Both C4-IL and C6-IL can be confirmed as metals according to their band structures.

In our present work, only the situation of a 4x4 AA-stacked graphene bilayer without any intercalated atom/functional-clusters is considered to demonstrate our nano-stitching method. In fact, such a nano-stitching method can also be applied to h-BN bilayer and graphene/h-BN bilayer with or without intercalated functional atoms or clusters. We believe that the nano-stitching method can be experimentally implemented in the future and it can provide us abundant 2D wormhole-like materials with different properties through changing the type of the bilayer, the species of the intercalated atoms/clusters, and the periodicity and size of the hole. Further theoretical and experimental efforts in this direction are expected to help to design and synthesize new 2D periodic nano-capsules with various encapsulated magnetic atoms or clusters for special applications.

**CONCLUSION**

We have proposed a nano-stitching method to modulate structures and properties of graphene and other 2D materials. A 4x4 AA-stacked graphene bilayer has been considered as an example to demonstrate the method with four stitched wormhole graphene allotropes of distinct interlayer connections. The structures, stabilities and electronic properties of the four wormhole graphene allotropes were investigated by first-principles calculations. We found that all of these wormhole graphene allotropes are more favorable than graphdiyne and dynamically stable, indicating that the nano-stitching method applicable. We expect that further theoretical and experimental efforts in this direction can help to design and synthesize new functional 2D periodic nano-capsules with various encapsulated magnetic atoms or clusters for special applications.
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