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Can graphynes turn into graphene at room temperature?

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ABSTRACT

The thermal stability of α-, β-, 6,6,12-graphyne and graphdiyne was studied by a statistic model, which was seriously tested by classical molecular dynamics (MD) simulations. By first-principle calculations of related potential energy curves (PEC), the model predicts that all the lifetime of free-standing single layer graphynes is more than 10^{44} years at room temperature. The sheets are predicted to be very stable even if the temperature gets up to 1000 K, but they quickly turn into graphene if the temperature is above 2000 K.

1. Introduction

As a fundamental element of life on earth, carbon can form numerous carbon allotropes consisting of three hybridization state (*sp*, sp^2, sp^3), such as graphite, diamonds, fullerene, carbon nanotubes and graphene [1–3]. Due to the distinct mechanical and physical properties, carbon allotropes have attracted tremendous attention, especially since the successful preparation of graphene. Because of its single-layer structure, graphene is expected to be a promising candidate to replace silicon for tinier and higher frequency transistor. However, graphene does not possess a bandgap [4]. and several methods have been proposed to open a bandgap, including application of uniaxial strain [5,6], control of the patterned hydrogenation [7], introduction of porosity [8], growth on substrates [9], and use of chemical doping [10] and so on. However, experimental realization of such schemes still remains a challenge [11].

Graphyne (also namely γ-graphyne), another allotrope of carbon, was first predicted by Baughman et al. in 1987 [12]. Replacing the acetylenic linkages ($-C\equiv C-$) in γ-graphyne with diacetylenic linkages ($-C\equiv C-C\equiv C-$) yields a new structure of carbon allotropes, graphdiyne, which was proposed by Haley et al. in 1997 [13]. Fig. 1 shows the structures of (a) γ-graphyne and its yne modifications, (b) α-, (c) β-, (d) 6,6,12-graphyne and (e) graphdiyne. Among these structures, graphdiyne and γ-graphyne are predicted to own a bandgap of 0.52 and 0.53 eV [14]. If the graphyne sheet is rolled into nanotube, β-GNTs present either metallic or semiconducting behavior and γ-GNTs present semiconducting behavior with a bandgap of 0.4–0.5 eV [15].

In the last decade, tremendous efforts have been made for the preparation of graphynes, but only some precursors and subunits of graphynes were synthesized [13,16–26]. In 2010, Li et al. reported that thin films of graphdiyne were successfully synthesized on copper surfaces and the film shows semiconductive properties [27]. Shortly afterwards, the same group synthesized graphdiyne nanotube arrays and graphdiyne nanowires [28,29]. Triggered by these experiments, a series of theoretical works have been made to

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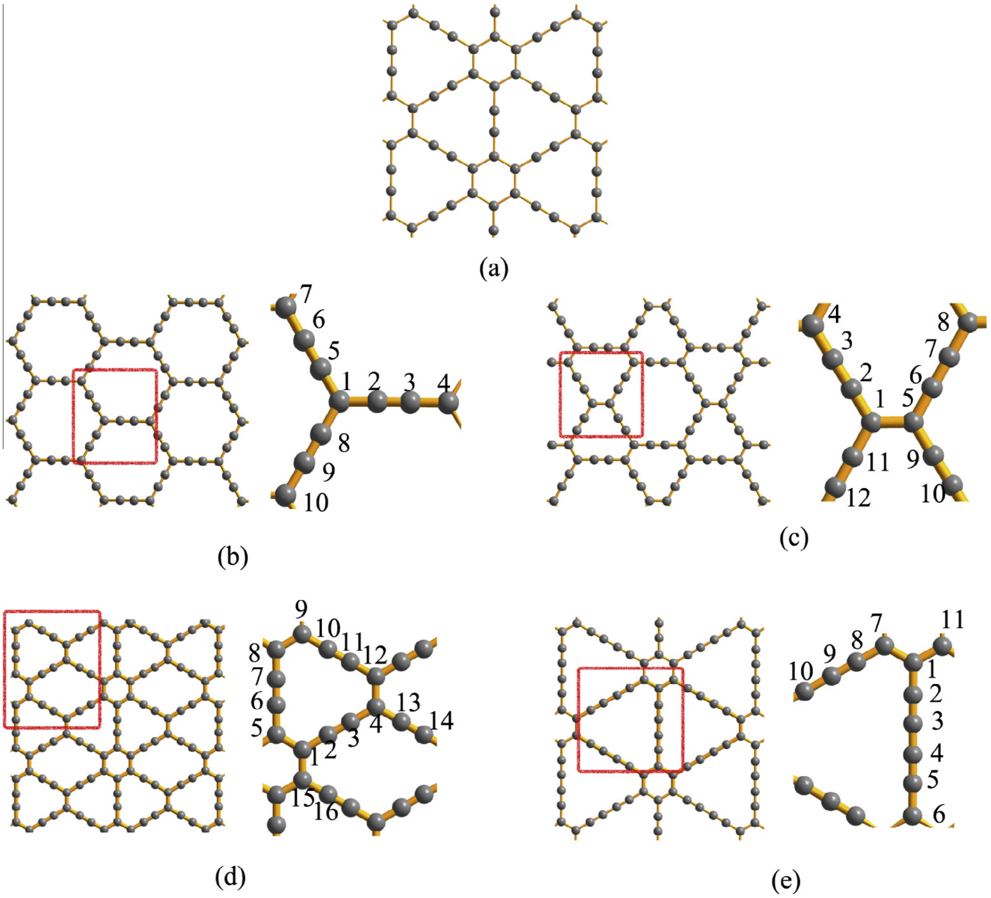

Fig. 1 – Optimized geometrical structure of (a) γ-graphyne, (b) α-graphyne, (c) β-graphyne, (d) 6,6,12-graphyne and (e) graphdiyne. (A colour version of this figure can be viewed online.)

predict the properties of graphynes in recent years. For example, first-principle calculations indicated that the bandgap of graphdiyne was about 1.2 eV [30,31], which was comparable to silicon, while the bandgap of γ-graphyne was about 0.96 eV and both can be modulated [31,32]. The other graphynes, such as α-, β-, 6,6,12-graphyne were predicted to have Dirac cones by first-principle calculations, and the cone of 6,6,12-graphyne was directionally anisotropic and nonequivalent [33], which was more versatile than graphene [34]. In addition, a lots of calculations showed that graphynes can be used for hydrogen storage and gas separation [30,35–37].

It is notable that synthesis of large homogenous sheets of single-layer graphyne have not yet been reported up to now and first-principle calculations show graphyne is less stable than graphene because the binding energy of graphyne is lower than graphene by about 0.56 eV/atom [35]. Accordingly, it remains uncertain whether free-standing graphyne can survive at room temperature, and how long it will survive before they turn into graphene at higher temperatures. These questions challenge current theories concerning the lifetime of nanodevices, the fatigue time and creep rate of bulk material and so on [38,39]. MD simulations seem direct solutions to this problem, but lifetime of most materials at room temperature is far beyond the time scale of MD simulations.

Very recently, a simple model based on the statistic of individual atoms was developed and has been successfully applied to predict the lifetime of carbon monatomic chains and single wall carbon nanocones [40,41]. In this work, this model was applied to predict the thermal stability of α-, β-, 6,6,12-graphyne and graphdiyne. Firstly, MD simulations with the empirical potential for C–C interaction were performed at higher temperatures to explore all possible paths for α-graphyne to turn into graphene, showing that several defects formed in graphyne will lead to formation of a hexagon, a subunit of graphene, and then avalanches of dislocation take place around the ring, and finally the structure of graphene forms. So the time taken by the formation of the primary defects should be the lifetime of graphynes. Secondly, we obtained the time taken by defect formation at higher temperatures separately by a great deal of MD simulations and by our statistic model with the same empirical potential in order to test the accuracy of our model. To apply our model, we calculated the PEC along minimum energy path (MEP) for the defect formation and used these data in the model to predict the time taken by defect formation. The results are in good agreement with the MD simulations. As a comparison, the harmonic transition state theory (TST) was also applied. Finally, for accurate prediction, first-principle calculations were performed to obtain the PEC along MEP for the defect formation for all the graphynes, and then their lifetime was predicted at any temperatures by our statistic model.