



Metamorphosis in carbon network: From penta-graphene to biphenylene under uniaxial tension



Obaidur Rahaman^{a,*}, Bohayra Mortazavi^{a,*}, Arezoo Dianat^b, Gianarelio Cuniberti^b, Timon Rabczuk^{c,*}

^a Institute of Structural Mechanics, Bauhaus-Universität Weimar, Marienstr. 15, D-99423 Weimar, Germany

^b Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, D-01062 Dresden, Germany

^c College of Civil Engineering, Department of Geotechnical Engineering, Tongji University, China

ARTICLE INFO

Article history:

Received 16 August 2016

Revised 6 December 2016

Accepted 7 December 2016

Keywords:

Phase transformation

Mechanical properties

Density functional theory

ABSTRACT

The power of polymorphism in carbon is vividly manifested by the numerous applications of carbon-based nano-materials. Ranging from environmental issues to biomedical applications, it has the potential to address many of today's dire problems. However, an understanding of the mechanism of transformation between carbon allotropes at a microscopic level is crucial for its development into highly desirable materials. In this work we report such a phase transformation between two carbon allotropes, from penta-graphene (a semiconductor) into biphenylene (a metal) under uniaxial loading. Using density functional theory we demonstrated that the phase transformation occurs through a synchronized reorganization of the carbon atoms with a simultaneous drop in energy. The results of this work confirms that penta-graphene is a *meta*-stable structure. On the other hand, a rigorous analysis of biphenylene suggests that it is an energetically, mechanically, dynamically and thermally stable structure, both in the form of a sheet and a tube. Its electronic structure suggests that it is metallic in both these forms. Therefore, this work unravels the possibility of phase transition in 2-D carbon systems and thereby designing nano-materials capable of altering their properties in an instant. Furthermore, heating biphenylene sheet at a high temperature (5000 K) revealed another phase transformation into a more stable *hexa*-graphene like structure. This proposes thermal annealing as a possible method of synthesizing one 2-D carbon allotrope from another.

© 2016 Elsevier BV. All rights reserved.

Introduction

The existence of allotropes in nature provides a fantastic opportunity for synthesizing alternative structures of desirable functions. Enabled by the versatile nature of carbon bonding, a rapidly growing number of experimentally isolated and theoretically predicted carbon allotropes are proposed as nano-materials suitable for interesting and unique applications. Graphene [1], phagraphene [2], penta-graphene [3], amorphized graphene [4,5], graphenylene [6–8] and Haeckelites [9–11] are among many of the proposed 2D carbon allotropes with notable electronic and mechanical properties [12–17]. Graphene, which is successfully synthesized in year 2004, is the strongest and most stable among all of them [1,18].

Although theoretical studies are valuable in understanding the structure-function relationships of these materials at a

fundamental level, the experimental synthesis of them still remain a challenge. The experimental synthesis of a predicted structure depends on many factors, specially its stability. Stability is a prerequisite for its formation as well as successful isolation from alternative possible structures. The experimental feasibility not only requires the structure to be at a local minimum on the potential energy surface but its neighboring minima corresponding to alternative structures should also be well separated by high energy barriers [19]. Moreover, the relative thermodynamic stabilities and phases of different allotropes of carbons remain mysterious [20].

Thus, understanding the relationship and possible transitions between the allotropes of a targeted material is essential for its experimental realization. Recently Zhang et al. predicted the existence of penta-graphene, a metastable new non-planar allotrope of carbon entirely consisting of pentagons [3]. It possesses both SP^2 and SP^3 hybridization, an unusual negative Poisson's ratio and an intrinsic band gap as large as 3.25 eV. They demonstrated the structure to be dynamically and mechanically stable and it could withstand a high temperature of 1000 K indicating that the penta-graphene phase was separated from other local minima on

* Corresponding authors.

E-mail addresses: ramieor@gmail.com (O. Rahaman), bohayra.mortazavi@gmail.com (B. Mortazavi), timon.rabczuk@uni-weimar.de (T. Rabczuk).

the potential energy surface by high energy barrier. The superior and remarkable properties of penta-graphene make it an attractive target of research in the field of nanoelectronics as evident from the numerous recent studies devoted on this allotrope [21–31].

Considering the highly desirable properties of this theoretically proposed carbon allotrope, an in-depth investigation of its metastable nature and the feasibility of its experimental synthesis is of supreme value. A recent computational study argued that the experimental synthesis of penta-graphene is rather improbable because of energetic funneling toward lower energy graphene structure with entirely sp^2 hybridization [19]. In fact, another molecular dynamics study demonstrated that upon uniaxial loading penta-graphene transforms into graphene through stable intermediates consisting of mixtures of pentagons and hexagons [32]. As opposed to this previous study, we report a rather sudden transformation of penta-graphene under uniaxial strain into what is identified as biphenylene [33–40]. The study was conducted using Density Functional Theory. Instead of the gradual and local transformation proposed by the force field study [32], the phase transition was found to be a global phenomenon where all atoms moved in unison.

The final product biphenylene not only has potential applications in various fields as stated below but it is also experimentally synthesized. Different oligomers of biphenylene were synthesized in the lab and characterized as synthetic targets for materials with interesting electronic properties [39]. Recently, an octafunctionalization method has been developed to fabricate and extend biphenylene structures into nanoribbons and sheets [36]. Biphenylene is predicted to be metallic in the form of a sheet or tube [38] but possessing a band gap in the form of ribbon [38] or by functionalization [35]. Biphenylene sheet can be used for hydrogen storage and in Lithium Ion Batteries (LIB) as it is predicted to adsorb lithium significantly stronger than graphene and graphyne [34]. A recent study suggested potential application of biphenylene-based nanoribbons in electronics and optoelectronics in the visible range [33]. Thus, in this work, a thorough characterization of the properties of biphenylene has also been carried out in order to explore its potential applications as a carbon nano-material.

Similar to the transformation observed in the 3D carbon system [41,42], this work demonstrates the possibility of phase transition in 2D carbon systems. It not only demonstrates possible pathways of synthesis for predicted 2D-carbon allotropes but also unfolds a novel paradigm in nanomaterials where the properties can be manipulated by phase-transition.

Methods

Vienna ab Initio Simulation Package (VASP) [43,44] was used to perform the *ab initio* and AIMD simulations within the framework of DFT. The exchange-correlation energy was treated within the Generalized Gradient Approximation (GGA) [45] using Perdew, Burke, and Ernzerhof (PBE) functional and Projector Augmented Wave (PAW) [46] method was used to calculate the interaction between the frozen core and valence electron. The 2D carbon network was separated from its periodic image by a vacuum of length 20 Å in the perpendicular direction. Energy minimizations were performed using conjugate gradient method with a threshold for total energy of 10^{-5} eV and atomic force components of 0.02 eV/Å. An energy cutoff of 450 eV and a k-point mesh size of $7 \times 7 \times 1$ in the Monkhorst-Pack scheme [47] were used for the Brillouin zone sampling. A higher k-point sampling of $30 \times 30 \times 1$ was used for the band structure and density of state calculations. For the AIMD simulations, a time step of 1 fs was implemented and Langevin thermostat [48] was used for maintaining the temperature. Phonopy [49] was used for the calculation of phonon

properties. Density Functional Perturbation Theory (DFPT) [50] as implemented in VASP and a high-accuracy energy convergence criterion of 10^{-8} eV was used for the calculation of atomic forces.

Results and discussions

Penta-graphene transforms into biphenylene under uniaxial strain

Penta-graphene under uniaxial strain is observed to undergo a sudden and global transformation into another allotrope of carbon. A supercell structure of penta-graphene consisting of 72 carbon atoms was constructed and minimized using VASP. Then the structure was treated with a gradual uniaxial strain applied step by step. At each step of the DFT calculation, the strain was incremented by 0.25% followed by an energy minimization with fixed size of the cell. During this process, the energy was observed to gradually rise until about a strain of 20%. At this point we observed a sudden drop in energy along with a global reorientation of the structure into an alternative allotrope of carbon composed of 4,6 and 8-membered carbon rings (Fig. 1).

The penta to biphenylene transformation that occurred within a single energy minimization step at 20% strain can be followed from Fig. 1 inset and a few intermediate snapshots, A, B, C and D. There were no distinct characteristics in these intermediates. They were selected only for the purpose of demonstration. One structure smoothly transformed into another during the energy minimization step. The penta to biphenylene transformation occurred as a global phenomenon rather than a local one as proposed by the force field study [32].

We note that penta-graphene has a non-planar structure with both sp^2 and sp^3 -hybridized carbon atoms (see the side view). During the penta to A transformation, all the sp^2 - sp^3 C–C bonds (but not the sp^2 - sp^2 C–C bonds) that were aligned in the direction of the applied strain dissociated. This created distorted and non planar (see the side view) 8-membered rings in the structure. In the following transformations A \rightarrow B, B \rightarrow C and C \rightarrow D, the 8-membered rings gradually became more symmetric while the structure remained non planar. This was accompanied by a significant drop in energy. The intermediates A, B and C were consisted of only 8-membered rings and nothing else. In the C \rightarrow D transformation, half of the 8-membered rings collapsed into a six-membered and a 4-membered ring by forming a C–C bond. The final step, D \rightarrow biphenylene was marked by a non-planar to planar transformation of the structure.

The stress in the structure responded to the increase in the strain in a similar manner as the energy. Before the penta to biphenylene transformation, the increasing uniaxial strain caused a gradual rise in the stress (Fig. S1). At strain = 20%, when the penta to biphenylene transformation occurred, a sudden drop in stress was observed. The sudden transformation of the non-planar penta-graphene to planar biphenylene structure seems to have caused the negative stress which was relaxed in the subsequent steps.

We note that the strain of 20% is close to the theoretical limit of graphene stretching under uniaxial strain [51]. In another study we compared the stress-strain curves of graphene, pentagraphene, biphenylene and a few other graphene-like carbon and carbon nitride networks under uniaxial strain [51]. Although the maximum stress attained during the stretching was highest for graphene, both pentagraphene and biphenylene demonstrated significant strength. We note that thermal fluctuations in the system can make the attainment of such a high value of strain difficult. In particular uniform distribution of the strain across the system is difficult to achieve in an experimental setup.

The final biphenylene structure was obtained by removing the strains and allowing the system to relax to its low energy local

Download English Version:

<https://daneshyari.com/en/article/8917863>

Download Persian Version:

<https://daneshyari.com/article/8917863>

[Daneshyari.com](https://daneshyari.com)