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Stability and dynamics of vacancy in graphene flakes: Edge effects

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ABSTRACT

Density functional theory calculations show that graphene flakes with monovacancy at the edge are energetically more stable than the flakes with vacancy in the middle. The energies of metastable and transition states for one step of vacancy motion towards the edge are calculated. We show that thermally activated motion of vacancy towards the edge occurs even at room temperature whereas the probability of return motion back to the middle is negligible. Molecular dynamics simulations of the vacancy motion in graphene flakes confirm this conclusion. The obtained results explain the mechanisms driving structural transformations in graphene.

1. Introduction

Experimental studies of the dynamics of individual carbon atoms in graphene have been empowered by the recent progress in aberration-corrected transmission electron microscopy (AC-TEM) capable of sub-Ångstrom resolution. The examples include AC-TEM observations of the formation and annealing of Stone–Wales defects [1], edge reconstruction [2,3] and formation of a large hole in graphene sheet from a single vacancy defect [3]. The AC-TEM has been also exploited in visualization in real time of the process of self-assembly of graphene nanoribbons from molecular precursors [4,5] and formation of nanometre size hollow protrusion on the nanotube sidewall [6]. Based on AC-TEM observations of transformation of small finite graphene flake into fullerene, a new 'top-down' mechanism for the formation of fullerene under the electron beam radiation has been proposed [7]. The critical step in the proposed 'top-down' mechanism of the fullerene formation is creation of vacancies in small graphene flake as a result of knock-on damage by electrons of the imaging electron beam (e-beam). The subsequent formation of pentagons at the vacancy sites near the edge reduces the number of dangling bonds and triggers the curving process of graphene flake into a closed fullerene structure [7]. Thus, dynamic behaviour of vacancies near graphene edge plays a crucial role in explaining mechanisms of the e-beam assisted self-assembly and structural transformations in graphene-like structures.

In a large (or infinite) graphene layer vacancy defects generated by the e-beam are stable at the time scale corresponding to *in situ* experimental conditions [8]. The formation and diffusion of vacancy defects in infinite graphene has been studied using a number of computational methods [9–13]. The structure [14,15], energetics [15] and electronic properties [16] of hydrogenated graphene flakes with a single vacancy have been also discussed in the literature. The terminal hydrogen atoms are only weakly bound to a graphene flake, and due to considerably smaller atomic mass they can be easily removed from the edge by the e-beam at experimental imaging conditions suitable for visualization of structural transformations in graphene-like nanostructures. This letter presents the detailed study of the structure, energetics and dynamic behaviour of vacancy near the edge of non-terminated graphene flakes.

Our density functional theory (DFT) calculations show that stability of small flakes with monovacancy in the middle increases as the vacancy gets closer to the edge. The directional movement of a single vacancy in graphene has been previously shown only in relation to the edge reconstruction [2] and coalescence of vacancies into a vacancy cluster [12]. The transition state (TS) search performed in this work allows us to elucidate the TS geometry and the energy barriers for the motion of vacancy near the edge and to predict that the directional motion of vacancy towards the edge should occur even at room temperature. The characteristics of the directional motion of vacancy towards the edge of graphene flakes have been obtained from classical molecular dynamics (MD) simulations. We conclude that vacancies tend to migrate to the edge of small flakes even during such fast processes as the e-beam assisted self-assembly and structural transformation of graphene-like structures in AC-TEM. A possible mechanism for graphene self-healing is also discussed.

2. Methods

The structure and total energy of perfect flakes and flakes with vacancies have been calculated at the unrestricted Kohn–Sham [17], 6-31G*/B3LYP [18] level of theory as implemented in Q-Chem

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quantum chemistry package [19]. The location of vacancy in graphene flakes with respect to the edge has a profound effect on its structure [20], so that the stable structure of monovacancy adopt either a 5/9- or a spiro-configuration. A 5/9 structure is generated by formation of an elongated carbon bond across the vacancy hole leading to creation of 5- and 9-membered ring. The 5/9 vacancy structure has radical character, and it is magnetic as it contributes an intrinsic magnetic moment of about 1 μ_B [21,22]. The spiro vacancy structure, on the other hand, does not contribute any unpaired electrons, and its structure differs significantly from the conventionally known 5/9 structure. The spin multiplicity of the metastable and transition states of small flakes with vacancy varies depending upon the size and symmetry of the flake. In all considered structures, the lowest energy states are found to be triplets. Vibrational frequency analysis has been carried out on the fully optimised structures to confirm the obtained metastable and transition states.

To study the dynamic behaviour of vacancies in graphene flakes canonical ensemble molecular dynamics (MD) simulations have been performed using GULP 3.1 software [23]. The carbon–carbon interactions are described using the Brenner potential [24]. The duration of each simulation run is 2 ns with 5 ps equilibration time. At room temperature, the rate of processes leading to bond rearrangements in carbon network is too low, which makes their simulation prohibitive to MD technique. To overcome this problem the elevated temperatures are commonly used in MD simulations, and we perform MD simulations at 2500 K. At 2500 K, vacancy moves readily from the middle to the edge of the considered flakes and infinite graphene nanoribbons. Yet this simulation temperature is less than that of 2700 K required for the direct transformation of graphene flake into a bowl-shaped structure at tens ns time scale [25].

The model C_{116} flake has been studied using both DFT and MD approaches thus allowing a direct comparison of the results obtained with *ab initio* and classical force-field techniques. C_{116} is the biggest flake studied using DFT, and the full set of the optimised structures obtained with DFT comprises C_{52}, C_{69}, C_{88}, C_{103} and C_{116} flakes, which are presented in Figure 1. A set of bigger graphene flakes, $C_{116}, C_{176}, C_{248}$ and C_{332}, and short rectangular flakes, $C_{395}, C_{447}, C_{623}$, with vacancy in the middle studied in MD simulations is shown in Figure 2. Additionally, the dynamic behaviour of vacancy in an infinite zigzag graphene nanoribbon with 22 rows of atoms in width has been studied in periodic boundary conditions. The width of the infinite ribbon was therefore kept the

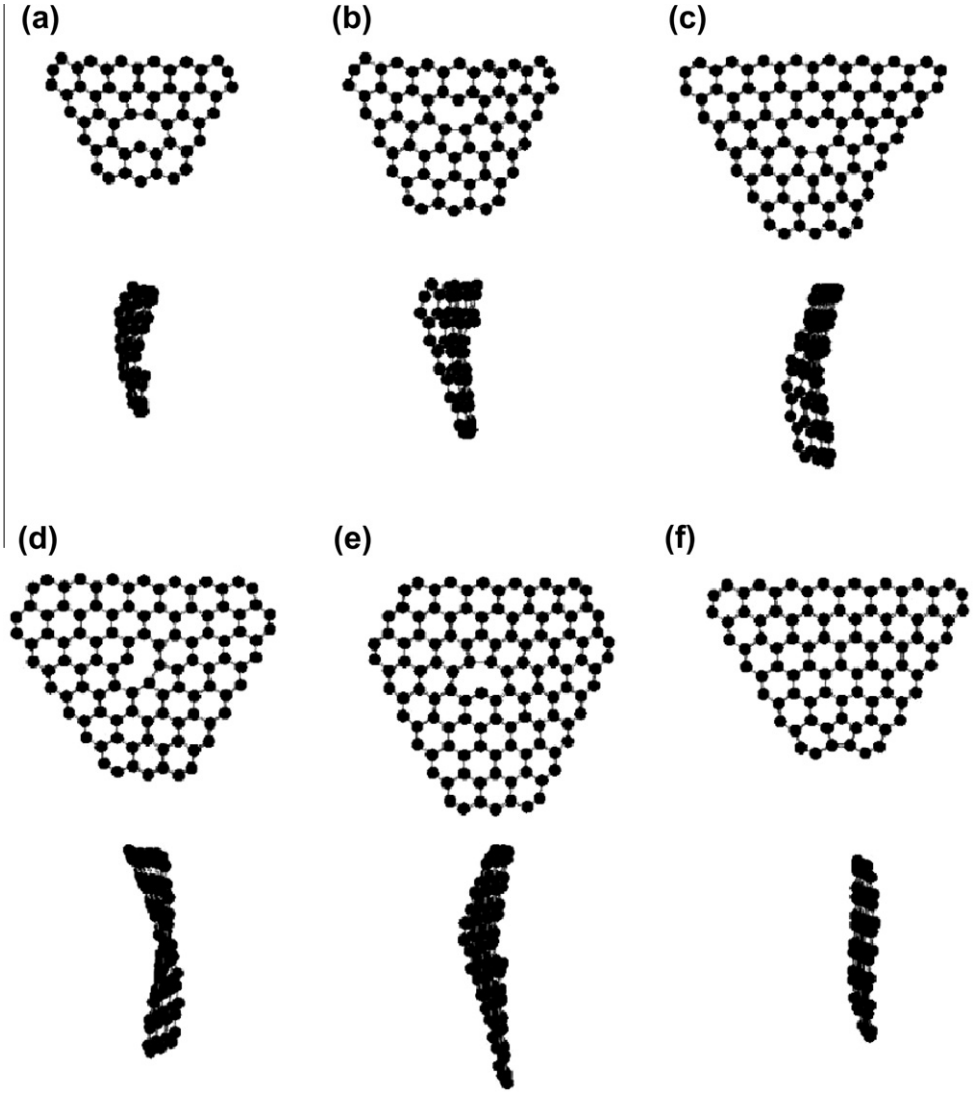

Figure 1. (a–e) The optimised structures of flakes with vacancy in the middle: (a) C_{52}, (b) C_{69}, (c) C_{88}, (d) C_{103}, (e) C_{116} and (f) the optimised structure of the C_{88} flake with vacancy at the edge. The side view corresponds to the flakes rotated by 90 degrees about the vertical axis in plane of the flake.