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Graphene healing mechanisms: A theoretical investigation

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ABSTRACT

Large holes in graphene membranes were recently shown to heal, either at room temperature during a low energy STEM experiment, or by annealing at high temperatures. However, the details of the healing mechanism remain unclear. We carried out fully atomistic reactive molecular dynamics simulations in order to address these mechanisms under different experimental conditions. Our results show that, if a carbon atom source is present, high temperatures can provide enough energy for the carbon atoms to overcome the potential energy barrier and to produce perfect reconstruction of the graphene hexagonal structure. At room temperature, this perfect healing is only possible if the heat effects of the electron beam from STEM experiment are explicitly taken into account. The reconstruction process of a perfect or near perfect graphene structure involves the formation of linear carbon chains, as well as rings containing 5, 6, 7 and 8 atoms with planar (Stone-Wales like) and non-planar (lump like) structures. These results shed light on the healing mechanism of graphene when subjected to different experimental conditions. Additionally, the methodology presented here can be useful for investigating the tailoring and manipulations of other nano-structures.

1. Introduction

Graphene, a two-dimensional carbon allotrope, has unique electronic, thermal and mechanical properties [1]. Originally, this material was obtained from graphite using an exfoliation process, called the “scotch tape” method [2]. Although this method yields pristine graphene samples, such a process is costly and not easily scalable. Presently, chemical vapor deposition (CVD) has been the most widely used process to grow graphene samples on a diverse set of substrates, such as steel [3], Ni [4,5], and Cu [6].

Graphene properties are extremely sensitive even to small modifications in its honeycomb structure [7]. Inherent defects from CVD growth processes represent obstacles to some technological applications, because they can degrade graphene electronic and mechanical properties. On the other hand, defects can be usefully exploited to obtain different properties for specific applications [8].

Recently, it was demonstrated that etched nanoholes of up to 100 vacancies on graphene membranes can be healed under low power STEM observation, even at room temperature [9]. The healing effect consists of the reconstruction (knitting) of the graphene structure. Carbon atoms from external sources near the hole region, eventually interact with its edges and can fill the vacancies. Hydrocarbon impurities near the membrane can also serve as a source for these extra carbon atoms. These nanohole fillings can occur with the formation of either non-hexagonal, near-amorphous, or perfectly hexagonal structures [9].

Other experimental works have also addressed the reconstruction of mono-vacancies and holes in graphene. Chen et al. [10] demonstrated the effectiveness of thermal annealing up to 900 ^{o} C (1173.15 K) to heal defects in graphene membranes. Kholmonov et al. [11] demonstrated defect healing in the top layer of multilayer graphene via CVD techniques using acetylene as a carbon feedstock and iron (Fe) as a catalyst at 900 ^{o} C (1173.15 K). The evolution and control of nanoholes in graphene by carbon atom thermal-induced migrations were studied by Xu et al. [12]. For temperatures around 525 ^{o} C (798.15K), graphene oxide (GO) can be healed and simultaneously reduced by methane plasma resulting in high quality graphene [13]. Moreover, self-repair mechanism during graphene sculpting by a focused electron beam were observed by Song et al. [14], while transformation of amorphous carbon into graphene was investigated by Barreiro et al. [15].

To address these healing and self-repair mechanisms, we carried out fully atomistic molecular dynamics simulations using the

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ReaxFF reactive force field [16]. Initially, we investigated the potential energy landscape near a graphene nanohole (defective regions) using a carbon atom as probe to estimate the energies involved during the healing process. Then, we carried out simulations at different temperatures (controlled by thermostats) to investigate the role of thermal energy in these healing mechanisms. Finally, we simulated the heating effects of an electron beam scanning to address the so called self-healing mechanism at room temperature reported by Zan et al. [9]. Our simulations show that graphene healing can be obtained by a simple annealing at high temperature in the presence of a carbon source. However, we could not observe the holes being filled at room temperature because of the energy barriers involved in the process. But if we take into account the electron beam heating effects in the simulations, the graphene healing at room temperature can be observed. In this case, either an imperfect or even a perfect hexagonal structure, depending on the specific energy rate for the beam heating, are obtained.

2. Methods and model

We carried out fully atomistic reactive molecular dynamics simulations (MD) using the ReaxFF force field [16], as implemented in the Large-scale atomic/molecular massively parallel simulator (LAMMPS) package [17,18]. ReaxFF is a reactive force field that allows the study of formation and dissociation of chemical bonds with lower computational cost in comparison to ab initio methods. ReaxFF parametrization is based on density functional theory (DFT) calculations and was successfully used to investigate many dynamical and chemical processes [19–21]. In the present work, we used the Chenoweth et al. (2008) C/H/O ReaxFF parametrization [22] and simulations were carried out with a time steps of 0.1 *fs*, with temperatures controlled through a Nosé-Hoover chain thermostat [23,24].

For comparison with ReaxFF results, we have also carried out some calculations using the Self-Consistent Charge Density Functional Tight-Binding (SCC-DFTB) [25,26] method, as implemented on DFTB + package [27]. DFTB is a DFT-based method and can handle large systems. SCC-DFTB is an implementation of DFTB approach that has the advantage of using Mulliken self-consistent charge redistribution (SCC), which corrects some deficiencies of standard DFTB methods [26]. In general, dispersion terms are not considered in DFTB methods and were included here via Slater–Kirkwood Polarizable atomic model [27].

The computational model used in our calculations consisted of a single-layer graphene membrane (aligned along the *xy* plane) with a hole (3.2 Å of radius) in its center. We considered two simulation scenarios: (i) the healing mechanism dependence on temperature and; (ii) mimicking effects of an electron beam scanning to trigger the healing mechanism at room temperature. Scenario (i) was implemented using temperatures ranging from 300K up to 2000K. For scenario (ii), in order to simulate the heat effect induced by the electron beam interaction with the system [28–32], we have applied a local heating protocol in which a rescaling of atomic velocities inside a cylindrical region is performed (see Fig. 1). The position of the heated region was varied during the simulations, thus mimicking the STEM experiments. Also, for both scenarios, we restricted the movement of atoms located at the edges of the graphene membrane by using virtual springs with elastic constants $K = 30 \cdot 0\ K$ cal/mol.Å. For scenario (ii) we also fixed the temperature in these atoms in order to dissipate the accumulation of energy. In our simulations, additional carbon atoms (called “added atoms” in the text and colored in red in all figures) with random kinetic energy values were deposited at random positions and at regular intervals of 500 *fs*.

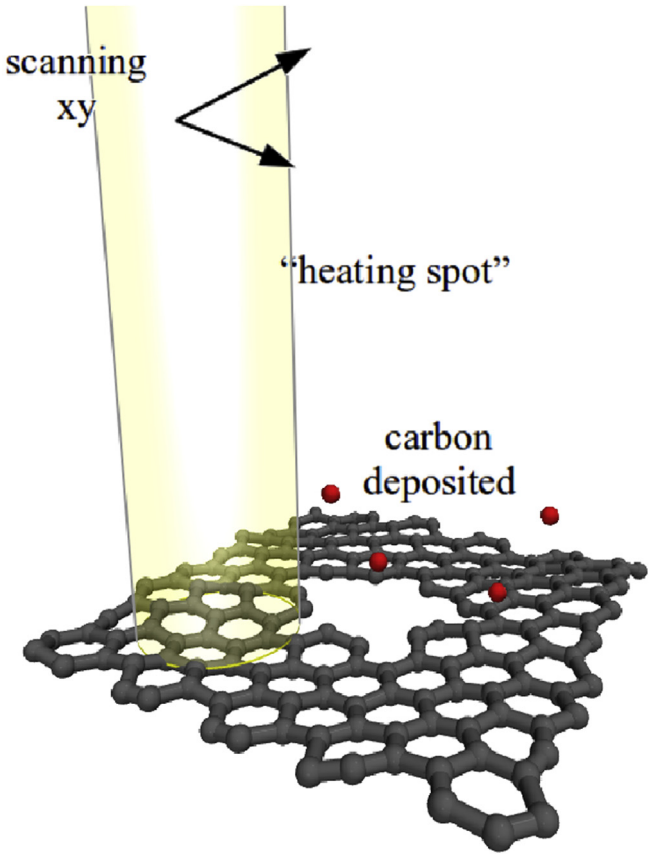

Fig. 1. Schematic representation of the computational model considered in our simulations. Local heating is represented by the yellow region, while added atoms (carbon atoms deposited) are represented in red.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Carbon depositions were made using single atoms, but we need to emphasise that depending on specific experimental conditions, several small hydrocarbons or other carbon species (C_2 and C_3) can be present. For instance, in a methane plasma [33] it is expected the presence of CH, CH2 and CH3 species in the environment [34]. However, in order to focus the investigation of the healing mechanism and speed up the molecular dynamics simulations, we opted to use only single carbon atoms for the deposition processes. The inclusion of other hydrocarbons, it would make necessary to consider other complicated questions, such as the activation energies and heat of formation for each considered species. These questions, despite of being interesting, would bring unnecessary complications to our analysis.

The local heating protocol adds a non-translational kinetic energy to the atoms in a cylindrical region centered along the z axis perpendicular to the graphene membrane (Fig. 1). The local heating scanned the membrane along the x and y directions, similarly to what is done by an electron beam in a STEM experiment. The effects of local heating with a cylindrical radius of 3.5 Å and energy rates between 0–3.0 *kcal*/(*mol.fs*) were investigated. If the energy rate per area is maintained constant, we can expect that changes in the cylindrical radius would not change the necessary energy rate to trigger the healing process. On the other hand, we expect that a small cylindrical radius would increase the necessary time of scanning to obtain a complete healing. All results presented throughout the text are representative simulations that illustrate typical results for the different processes of the graphene healing mechanisms.