Controlled healing of graphene nanopore

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Abstract

Nanopores – nanometer-size channels hold significant promise for numerous applications: DNA sequencing, sensing, biosensing and molecular detectors, and catalysis and water desalination. However, these applications require accurate control over the size of the nanopores. Since graphene is often mentioned as a promising material to host nanopores, we have performed realistic computer simulation studies of regrowth and healing of graphene nanopores of different sizes ranging from 30 to 5 Å. Our simulations clearly point to at least two distinct healing mechanisms for graphene sheets: edge attachment (where carbons are attached to the edges of the graphene sheet/pore) and direct insertion (where individual atoms insert directly into a sheet of graphene, even in the absence of the edges.) The insertion mechanism is a surprising prediction that points to the growth process that would be operational in pristine graphene. We have uncovered an unusual dependence in the speed

of nanopore regrowth and the structure of “healed” areas as a function of its size in a wide range of temperatures. Our findings point to significantly more complicated pathways for graphene annealing. They also provide an important enabling step in the development of graphene-based devices for numerous applications in nanotechnology. Our results suggest the possibility to control the final size of healed nanopore by terminating the annealing at a prescribed time dependent on the temperature.

Key words: graphene, nanopore, healing mechanism, simulation

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1 Introduction

The recent discovery of graphene has revolutionized material science and attracted the close attention of the materials science community [1,2]. A significant next step in the evolution of this field will be the development of reliable, reproducible, and well controlled techniques to produce engineered nanostructures with graphene as a key functional element. One example of such a nanostructure is a graphene nanopore. Nanopores have emerged as powerful functional devices for many applications: it has been argued that graphene nanopores can be used for DNA sequencing [3], detection of single molecule [4], biosensing [5,6], and water desalination [7] to name a few. Modern experimental technology, such as electron beam drilling [8], limits the minimum diameter of nanopores to 2-5 nm [9,10], while for example water desalination requires nanopores of maximum size 0.55 nm [7]. In addition,

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damage from the electron beam yields undesired amorphization of the crystalline lattice structure around nanopore [11], which changes the electronic properties of graphene nanodevices. A frequently used method of graphene healing is annealing of the sample in the ambient conditions at high temperatures with a supply of extra carbon atoms [9]. The atoms then attach to the graphene structure and regrow the pores. While this process is understood empirically, it is useful to provide a more detailed microscopic description of the regrowth and healing process.

To fulfill the promise these devices hold, the field has to make the next significant step in nanostructure preparation such as production of controlled nanometer sized pores with controlled properties. The latter step in the preparation of the pores is a complicated process and its investigation is still in its infancy. We anticipate a significant and growing demand for techniques that produce size-controlled graphene nanopores [12,13]. In this article, we investigate the details of graphene growth in the presence of a supply of carbon atoms. We have studied the regrowth and healing of graphene nanopores by means of molecular Monte Carlo (MC) simulations in various temperature and pore size conditions. We found, somewhat unexpectedly, two distinct healing mechanisms of the nanopore. The first, fully expected one, involves reconstruction of the lattice at the open edges of the pore, where carbon atoms approach and attach at the edge. This mechanism is active as long as the nanopore edge exists and at all temperatures. The second mechanism operates when the temperature is above an estimated critical $T_c = 900$ K. It is best described as the insertion of carbon atoms directly into the crystalline structure of graphene. These insertions result in the formation of the defects that slowly drift towards the nanopore edge. The second mechanism is present

in the absence of any edges and therefore operates even in a pristine graphene sheet. Below, we study regrowth and healing of graphene nanopores by means of molecular Monte Carlo simulations in various conditions in the NPT ensembles (constant number of particles N , constant pressure P and constant temperature T) with periodic boundary conditions in the plane for samples of $N = 4032$ before the creation of nanopore.

2 Healing mechanisms

To simulate the healing of the nanopore, we inject carbon atoms in groups of 32 or 18 in the free space above and below free-standing graphene sample. We need to provide additional carbon atoms manually, because we removed all the residuals which may be left after drilling. In reality, the supply of carbon atoms can come from additionally injected atoms during the healing process, or from the carbon remains which were not completely removed after drilling. The addition of carbon atoms does not impose any limitations on the healing mechanisms. Before starting the simulation, we ensure that no two atoms are close enough either to become immediately bonded to the graphene sample or to each other. We focus on the growth of a free-standing graphene.

2.1 Edge healing

Approximately half of the atoms at the edge have few than 3 neighbors, which results in the presence of dangling bonds. When a carbon atom appears in the close vicinity of the edge of the nanopore, it bonds to the edge (see Fig. 1A). Edge reconstruction proceeds by forming a new ring of carbon atoms as shown

in Fig. 1B, or a dangling atom. Subsequently, a new carbon atom will frequently be attached in the close vicinity of the previous one (see Fig. 1C). Figure 1D shows the result of the reconstruction of the edge. This process repeats many times, thus reconstructing the structure of the graphene lattice, healing the nanopore and reducing its size [14,13,16]. In another less frequent scenario for edge healing, we observed the formation of a chain of carbon atoms attached to the edge of the nanopore (shown in Fig. 1E.) It is observed that the longer the chain becomes, the less stable it is. After a short time (from one to ten thousand of Monte Carlo steps depending on the temperature and chain length) the chains become a part of the structure of graphene sample. In this case (Fig. 1E), we can see the formation of a defect structure with rings consisting of five and seven atoms. The structure developed is “half” of Stone-Wales defect, well known for graphitic structures.

This mechanism works as long as the open edge is present, or in other words, as long as the nanopore exists. The fact that new atoms attach to the dangling bonds means that both the absence of the energy barrier and the healing rate will be practically unaffected by the temperature. Therefore, edge healing of graphene nanopores is limited mainly by the carbon supply rate, and is actually a manifestation of the graphene crystal growth [15,13,16], which is natural and has been studied in detail. The analog of this process is known for 3D crystal growth. Similar to 3D crystals, which grow layer by layer [17], we find that the 2D crystal (graphene) is growing line by line.

The observed formation of chain events are (Fig. 1E) relatively rare. In the most cases, atoms attach to the edge one by one, with the reconstruction of the edge after each event. In several cases, we observed that small chains can reach 10-15 atoms in length and become a “center of condensation” for other

Fig. 1. The edge healing mechanism: A) a free carbon atom attaches to the open edge; B) edge reconstruction - new ring of carbon atoms is formed; C) second atom attached in the vicinity of the previous one; D) new edge reconstruction; E) formation of a chain of carbon atoms; F) reconstruction of the edge and formation of new 5 and 7 rings using the atoms of the chain.

carbon atoms and a starting point for the reconstruction of a relatively big area of graphene. This results in an asymmetry of the healed nanopore shape, see Fig. 2. The structure of the reconstructed lattice is not ideal, albeit more ordered than amorphous state. The type and number of defects depend on the temperature of the healing. This will be discussed in more detail later.

Again, similar instabilities are also observed for 3D crystals [18,19] and often results in dendritic growth. In 2D world, a “finger-like” instability of a free surface is a common phenomenon in much more complex biological systems. For example, the collective motion of epithelial cells during wound healing occurs via fingering destabilisation of the border [20] and results in a similar structure as in Fig. 2. We believe that such similarities would be more noticeable for nanopores of bigger sizes.

Fig. 2. Part of the asymmetrically healed nanopore with a “finger-like” protrusion in the healed area. Initial nanopore diameter was 4 nm, and healing temperature was 2100 K.

2.2 *Atoms insertion crystal growth*

From the Monte Carlo simulations, we observed a second healing mechanism called atom insertion. This occurs when an atom inserts directly into a graphene plane. This mechanism is only accessible for 2D crystals, to the best of our knowledge, was never reported for 3D crystals. When a carbon atom appears in the vicinity of the graphene plane, but away from the edge of the nanopore, the atom will bond to the surface of graphene sample forming adatom defect (Fig. 3A). This configuration tends to become more energeti-

cally favorable (energy gain $\Delta E = 1.2$ eV), if the temperature is high enough to overcome the energy barrier. The previously attached atom becomes bonded to two adjacent carbon atoms in the graphene plane, breaking the initial bond between them and forming two 7-rings (instead of two 6-rings). This topological defect is shown in Fig. 3B. We found that the energy barrier separating the configurations in Figs. 3A and 3B is $\Delta E = 1.85$ eV, which is relatively high. As a result of this barrier, the transition between states does not occur if the temperature is below $T_c \approx 900$ K. After the defect is formed, it can easily move inside graphene plane in any direction as shown in Fig. 3C. The motion of the defect is similar to the Brownian motion of a particle.

A vector pointing to the nanopore from the place where the atom was initially attached indicates the general direction for the motion of the defect. Fig. 3D shows the atomic configuration of the same area after 15000 MC steps. Here, we can clearly see that: i) at the initial position, where the new carbon atom has been attached, is a perfect lattice; ii) the defect moved approximately $10 \text{ \AA}$ to the left and up, towards the nanopore.

This mechanism is unique for 2D crystals and has no analogy for 3D. Insertions of the atom means breaking of the in-plane bonds, and distortions of the crystalline structure around. If a similar mechanism would be possible for 3D crystals, it would mean the formation of dislocations in an already grown layer. It is extremely energetically expensive, because it globally affects the bonds of many atoms in the layer where the defect is forming with the layer(s) below. Conversely, for 2D crystals it mainly affects the local atomic bonds in close vicinity to the insertion point. Thus, for a 2D crystal like graphene, atom insertion is possible due to flexibility of the graphene lattice, and the possibility to curve in a third dimension with local (non-global) effects on

Fig. 3. The surface healing mechanism: A) a free carbon atom binds to the graphene surface; B) the formation of a topological defect which consist of two 7-rings; C) the newly added atom “displaces” original atom (marked with red dot), defect starts to move; D) position of defect (marked with red dot) after 15000 steps, defect moved ≈ 10 Å left-up from the initial position towards the nanopore.

atomic bonds.

The formation of adatom defects similar to shown in Fig. 3 are well-known for graphitic structures [21–23]. There is a difference between defect in Fig. 4 and abovementioned articles. In our case we observe breaking of the initial bond between two adjacent carbon atoms and formation of new bonds with the adatom, thus each atom will still have 3 neighbours and the adatom becomes an in-plane atom. This contrasts with the other studies [23,22] where the adatom stays in a “bridged position” on the surface of graphene sheet. We also show that these defects are playing an important role in the healing of graphene nanopores.

Another noticeable feature observed in our simulations were “walking atoms”. A carbon atom attached to graphene plane can easily move on top of the graphene lattice without inserting into it. These “walking atoms” are very noticeable if the temperature is around 900 K or lower. In this case, there are two possibilities: 1) the atom will finally move into the graphene plane (thus starting insertion growth), or 2) during the walk it will reach the edge (thus contributing to edge growth). “Walking atoms” can also be seen in some real-time movies in the supplementary material of article by Dekker and others [12].

In reality, all observed healing mechanisms work simultaneously. The relative importance of each of them depends on the size of the pore and temperature. The smaller the size of the nanopore - the greater the role played by the surface healing. Moreover, even when the nanopore is nearly healed, atoms will still bind to the surface. This introduces defects in the crystalline structure.

3 Healing rate

The healing rate of the nanopore is directly proportional to the supply rate of carbon atoms in the sample. In addition, the attachment rate will depend on the temperature. We will present the result assuming constant supply rate in all of our simulations.

To determine the quantitative behavior of the healing rate, we increase of the number of carbon atoms with respect to the number of Monte Carlo steps, or Monte Carlo time $\partial N / \partial t \propto \partial S / \partial t$, where S is healed area. As described above, at temperatures below $T = 900$ K, the healing rate drastically decreases,

because the atom insertion mechanism ceases to work, and the carbon atoms that are attached to the graphene surface rarely get involved into healing. Thus, we used the healing rate at $T = 900$ K as a normalization, and express healing rates at other temperatures with respect to the healing rate at $T = 900$ K.

Figure 4 shows the relative average healing rate for different simulation temperatures. For every temperature, the presented result is an average of 20 to 40 simulations for every studied nanopore diameter. From this, the healing rate is linearly proportional to the temperature and increasing with the healing temperature. We also found that the healing rate is essentially independent of nanopore size. Geometric considerations show that, $\partial S/\partial t \propto R\partial R/\partial t$, and thus $\partial R/\partial t \propto 1/R\partial S/\partial t \propto 1/\sqrt{(S)}\partial S/\partial t$, where $R \propto \sqrt{S}$ is characteristic size of the pore. Constant healing rate $\partial S/\partial t$ meant that radial healing $\partial R/\partial t$ rate increases during healing. This increase in radial growth rate as $R \rightarrow 0$ has a significant implication for any process that requires a precise control of graphene edge in the final stage or if the target size of the pore is small.

4 Structure of the healed nanopore

We observed the structure of the healed area and how it depends on the healing temperature. Figure 2 shows the reconstructed structure of the graphene sample. It is easy to notice that the reconstructed area is not perfect and consists not only of hexagons, but also of pentagons, heptagons and octagons. In a perfect graphene sample carbon atoms are arranged in a honeycomb lattice and each atom is connected to three its nearest neighbors. Therefore, imperfections can be described as a number of non-hexagons with respect to the

Fig. 4. Relative healing rate $\partial S/\partial t$ as function of temperature.

number of hexagons in the structure.

Figure 5 shows the number of “rings” of different types in the healed area for a sample with nanopore of $R = 2$ nm which was healed at $T = 1500$ K. For healing temperatures 900 and 1500 K, the number of hexagons (“R6” rings) is approximately 40% of the total number of structural rings in the healed area, the number of heptagons (“R7”) and octagons (“R8”) together is equal to approximately 15-20% of the total number of rings and the rest of the area consists of pentagons (“R5”). Increasing the healing temperature to 2100 K results in significant changes to these structures: the number of “R6” rings grows to approximately 60% in the cost of “R5” rings. Thus, increasing the temperature results in more “graphitic” quality of the healed area.

The area outside of the nanopore is also affected by the healing process due to the insertion healing mechanism. It results in the formation of heptagons

Fig. 5. Structure of healed area, sample size $100 \times 100 \text{ \AA}$, initial nanopore radius $20 \text{ \AA}$.

(“R7”) in the cost of hexagons (“R6”). Unlike the structure of the healed area, this process is practically unaffected by temperature, the number of R7 rings is directly proportional to the healing time, if temperature is above 900 K.

5 Conclusions

The ability to control annealing and healing of graphene is an essential next step in the future applications of the graphene-based materials. With significant attention drawn to the technological applications of graphene, the details of graphene annealing are in its infancy. Through the analysis of Monte Carlo simulations, we have found at least two healing mechanisms for graphene: 1) the edge growth mechanism is fully expected from previous discussions in the literature [15,13,14], and 2) the “atom insertion” mechanism, where atoms

are directly inserted into graphene layer once they can overcome the energy barrier for bond formation, typically at temperatures higher than 900 K.

We verify the natural expectation that the rate of nanopore healing is significantly affected by temperature and increasing linearly with T , at least within available MC data. Therefore, our results suggest the possibility to control the final size of healed nanopore by terminating the annealing at a prescribed time dependent on the temperature.

We can point to two parameters that are critical for the control of the healing process: the supply of carbon atoms and the temperature of the healing process. The healing temperature is one of the most important parameters to control, because healing rate is significantly affected by the temperature. Moreover, healing can continue even in the absence of carbon supply at the cost of internal structural defects, if the temperature is high enough.

Our simulations do confirm that healing is a statistical process that tends to produce high asymmetries in re-grown pores (see Fig. 2). This statistical irregularity can itself be a factor that would limit the quality of healed nanopores and therefore this aspect might limit applicability of this healing method for potential applications that use controlled-sized graphene nanopores, especially when the pores are small.

The structure of the healed area is irregular with a number of pentagons and heptagons being produced, indicating significant changes of graphene sample. In turn, it means that the electronic structure is also altered. Taking into account the importance of the electronic structure for any nanopore related application, further study would be required to understand the influence of structural imperfections on local electronic properties like transport, tunneling

conductivity and others. We find that the number of pentagons and heptagons is not equal, indicating a change in the topology that would lead to a change in the shape of graphene.

A Methods

In our simulations, we study graphene by means of molecular Monte Carlo simulations. The atomic displacement for each trial of MC step was chosen in such a way that the acceptance rate for every move is between 0.4 and 0.5. The interatomic interactions are calculated with the LCBOPII potential [24] that we have shown describes the elastic and thermal properties of graphene [25,26]. It is important to note that this potential allows bond breaking and formation with realistic energy barriers. Also it gives a significantly better description of the lattice dynamics [27] than the Tersoff potential [28].

We perform MC simulations at finite temperature T and constant pressure $P = 0$ with periodic boundary conditions for a sample of $N = 4032$ atoms (ideal sample, without nanopore) with equilibrium size at zero temperature of 10.33 nm in the x direction and 10.224 nm in the y direction. The size of the simulation box in z -direction was set to 10 nm. To maintain the constant pressure $P = 0$ sample size fluctuations were allowed in all directions (x , y and z).

Nanopores have been created in the following way: first, atoms within the circles of pre-defined radius (from 5 to 30 Å with the step of 5 Å) have been removed. Second, the sample was annealed at $T = 4200$ K to simulate the damage induced by the electronic beam at the edges of the nanopore. This

Table A.1

Parameters of the samples used in simulations

R, nm	Number of atoms removed	Atoms left
0.5	28	4004
1.0	122	3910
1.5	270	3762
2.0	474	3558
2.5	748	3284
3.0	1080	2952

temperature is a bit lower than the melting temperature of graphene [29], and thus can give edge structure similar to that obtained during drilling. Finally, samples were cooled to $T = 300$ K and re-equilibrated at this temperature. Table A.1 shows parameters of the obtained samples, with radii 5, 10, 15, 20, 25 and 30 Å.

To simulate healing, carbon atoms were added randomly in small groups of 9 or 16 atoms at both sides of the sample (a total of 18 or 32 atoms in each series). In both cases atoms were added at a random height from 3 to 8 Å below or above the sample spread over an area 21x21 Å or 40x40 Å for the first and second cases respectively. It was checked that minimum distance between atoms was at least 3 Å, ensuring that no two atoms can become immediately bonded with each other or to the sample. The atoms were added relatively close to the graphene sample to speedup simulations. In general, atoms can be added far away from the graphene sample, but such procedure significantly

increases simulation time. After the atoms were added, the evolution of the system was simulated for 50000 MC steps. This number of steps is enough for the system to reach new equilibrium state.

After finishing the simulation, a new series of atoms were added as described above, and the system was run for a new 50000 steps. This cycle was repeated until the nanopore was completely healed or until the pore reached the required size. After finishing the complete healing cycle, the structure of the sample was analyzed as described in *Structure of the healed nanopore* section of this paper.

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