Computer Simulations and Study of Bridge-Like Radiation Defects in the Carbon Nano-Structures in Composite Materials

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ABSTRACT

We perform computer simulation and study of a special type of bridge-like defects in carbon nanostructures, which can be produced under fast electrons and ions irradiation. The binding energy and structure characteristics of the defects in carbon nanotubes and in graphene have been determined using known semiempirical extended Hűckel techniques.

Keywords: computer simulation**,** carbon nanotube, graphene, bridge-like defect, radiation effects

1 INTRODUCTION

Carbon nanotubes and graphene attract great attention of scientists and engineers because their unique mechanical and physical properties. In particular, single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNT) can be used in production of composites. These composites can be based on metal, ceramic or polymer matrices filled with carbon nanotubes as elements of reinforcement. Many of the good physical and electrical properties can be exploited by incorporating the nanotubes into some form of the matrix material [1-4]. Obviously the main goal of using nanotubes in making composites is using their extremely high mechanical properties in combination with low density. The same is true of the very high electrical conductivity of especially the SWNT where normally insulating polymers can be rendered conducting with very low weight percent of the nanotubes. This situation unfortunately is not true of the very high thermal conductivity of the carbon nanotubes. Composites produced from carbon nanotubes only yield thermal conductivities following the rule of mixtures. One of the important and unfortunately poorly understood factor is being a way of bonding of a matrix with carbon nanostructures. It should be taking into account that the sp^2 electron structure often results in very low binding energy between CNT's surface and atoms of many elements. This results in poor interfacial bonding of the nanotubes or nanostructures fragments that can slide in the matrix, or relatively to each other under stressed condition. It results in decreasing the part of CNT's surface, transferring stress between matrix and reinforcement elements under stressed state of the composite. This therefore limits rather severely the amount of ultimate strength present in the nanotubes that can effectively be transferred to the matrix. It is reasonable to suppose that defects in such structures might improve situation by linking nanoelements to each other allowing them to act as cross-links which will increase the stiffness of the composite. In general, investigations of radiation effects in carbon nanostructures are of great interest at present [5-7]. It is not yet well understood which kinds of stable atomic complex defects exist in carbon structures and it is not easy to observe such defects directly and to make interpretation of measurements [8]. In this situation computer simulation of radiation defects in carbon nanostructures becomes of great importance [9-12]. It is posited, that some types of radiation defects can act as a route to additional chemical bonds, promoting the strengthening of composite materials consisting of high concentration of carbon nanostructures. In this paper we consider results of simulation and investigation of structural and energetic properties of some possible configurations of defects, which can be produced by fast particles irradiation of a nanocomposite, involving carbon nanostructures. We used for calculations the well known semiempirical atomic basis extended Hűckel method.

2 SIMULATION

Further we consider different types of possible radiation defects in carbon nanostructures rising under irradiation. We imply that all carbon species will be introduced into some matrices and focus our attention on possible effects of

binding carbon nanospecies in stiff clusters for the limitation of relative displacement and stiffening the materials.

Figure 1 presents a possible bonding configuration built between two parallel SWNT (6,6) with a bridge-like bond, which can be produced under ion-, fast electrons or neutron irradiation. We considered a case, when vacancies were produced in both carbon nanotubes in such a way, that vacancies were faced each other and the interstitial atom *i* was placed between them. The calculation was performed with using energy minimization of the defect zone.

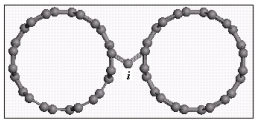

Figure 1. A bridge-like defect linking carbon nanotubes

After minimization procedure the binding energy of the configuration was obtained as large as 3.9 eV for every bond of bridge-like configuration

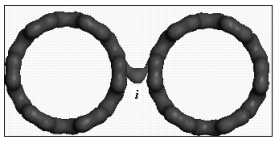

Figure 2. Electron charge distribution for the configuration presented in Fig.1

Figure 2 presents the electron charge distribution for the defect in Fig.1 by the electron density equals 1.4 el/Å^3 . It should be noticed, that it is a typical electron charge density for carbon nanostructures , corresponding to covalent bonds. So that it proves a fast bridge-like bond, rising between two nanotubes.

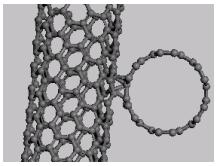

Figure 3. The linking defects between crossing nanotubes

Figure 3 presents the linking defects between two crossing nanotubes with total binding energy equal to 9.3 eV.

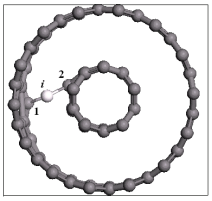

Figure 4. Atomic configuration of an inner bridge-like defect in a two-walled carbon nanotube. The interstitial atoms here and below are distinguished by light.

Figure 4 presents a bridge-like defect which can be produced under irradiation of a system, involving multi-walled carbon nanotubes. In this case we performed the calculation for the two-walled nanotube with the inner tube (5,0) and the outer tube (14,0). Diameters of CNT's (5,0) and (14,0) are equal to 3.9 Å and 10.9 Å accordingly. The inside between for this two-walled nanotube equals to 3.5 Å and is close to graphite interlayer distance.

In our simulation the vacancies in both inner and outer nanotubes were faced each other and the interstitial carbon atom *i* was placed symmetrically between the vacancies. The configuration, arising after using the energy minimization, is shown in Figure 4 . One can see that some atoms, closest to vacancies have moved slightly into the gap between the nanotubes. This movement is necessitated to facilitate the creation of the bonding bridge between the inner and outer nanotubes. For example, the distance between atoms 1-2 equals 2.49 Å , between *i* - 1 : 1.56 Å , *i* - 2: 1.49 Å . In this case the angle between bonds is very near to 180^o. The total binding energy of the *i* atom equals -4.7 eV.

We proposed, that the open ends of carbon nanotubes in principle can also serve as bonding sites for knocked out atoms. A possible configuration with a bridge-like single end-bond, based on the interstitial *i* rising between the external and the inner tubes is presented in Figure 5. After the relaxation of the structure was performed, the binding energy of the defect was equal to 10.0 eV.

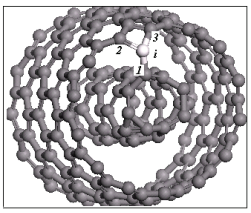

Figure 5. A possible atomic configuration of a single bridge-like defect between the ends of a two-walled carbon nanotube (5,0) / (14,0). The interstitial is marked by light. Lengths of the bonds: *i*-1: 1.31 Å ; *i*-2, *i*-3 : 1.41 Å .

The rather unusual nanotubular object is presented in Figure 6. It involves 5 bridge-like end-bonds between the external and the inner tubes. Such defect results not only in bonding, but also in closing the end gap of two-walled carbon nanotubes.

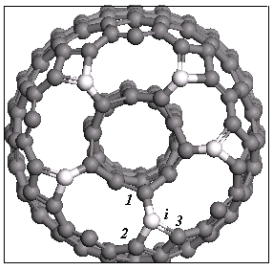

Figure 6. View of the atomic configuration of the complex bridge-like defects. Lengths of bonds: $i - 1$: 1.30 Å , $i - 2$, $i - 3$: 1.39 Å . Distances between interstitial atoms vary approximately from 3.5 to 4.1 Å .

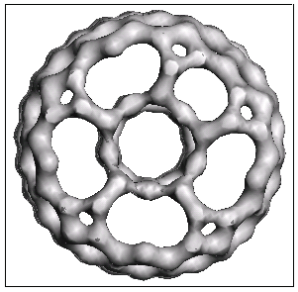

Figure 7. Electron charge distribution for the defect presented in Fig.6.

One can see in Fig.7 the electron charge distribution for the defect presented in Fig.6 by the electron density equals to 1.4 el/Å^3 . The calculations were made also for bilayer graphene fragment, in the usual graphite-like stacking configuration presented in Figure 8. The coupled atom pair removed by creating the vacancy pair is marked by black.

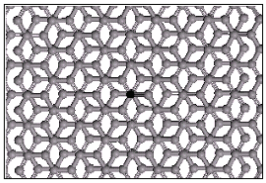

Figure 8. Graphite-like bilayer graphene used for making coupled vacancies

The interstitial atom *i* was placed between them. After that energy minimization procedure was used to obtain a configuration with minimum value of the total energy of the defect volume. During the minimization the edge atoms of graphenes were fixed in order to account the size effect of a larger graphene sheet. One can see from Figure 9 that after relaxation the center parts of graphenes near the defect significantly entered into the gap. The distances between atoms 1-2 and 3-4 turned out equal nearly 1.43 Å , that approximately are the distances in ideal graphene structure and the arising of additional bonds between graphenes was expected.

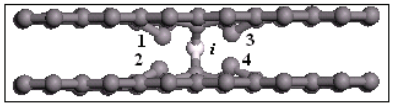

Figure 9. The bridge-like defect in the central part of two-layer graphene

The distribution of the electron charge presented in Figure 10 by the charge density 1.4 el/Å^3 proves existing of two additional covalent bonds between graphene layers together with primary one, created by the interstitial atom *i*. The total binding energy for this defect configuration was calculated as large as -11.3 eV.

Figure 10. The distribution of the electron charge in the configuration presented in figure 9.

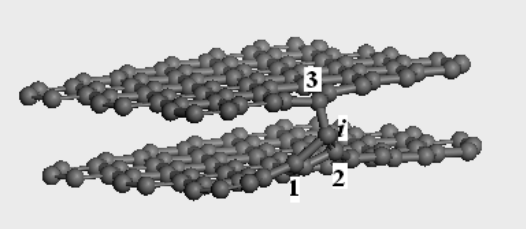

Figure 11. The bridge-like defect based on an interstitial atom *i* at the end of bilayer graphene.

Result of modeling of end -bridge-like defect for graphene sheet is presented in Fig.11. One can see a significant deformation of graphene fragments near the defect zone. The binding energy of the interstitial at this configuration was equal to -9.3 eV.

3 CONCLUSION

Some possible types of stable bridge-like radiation defects, which can originate under fast particles irradiation in typical carbon nanostructures were simulated and calculated using known semiempirical extended Hűckel techniques.

Results of calculation illustrate possible linked configurations for SWNT, MWNT, graphene. The binding energy and structure characteristics of defects have been determined. A new type of defect configuration based on bridge-like bonds between ends of MWNT is presented. Radiation production of such types of defects can be useful for application in materials science, particularly in R&D of new materials with using the carbon nanostructures as reinforcement elements, for stiffening the nanostructures and modifying physical characteristics like electrical- and heat conductivity.

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