



STRUCTURAL MODELLING OF NANO-CARBONS AND NANO-CHALCOGENIDES

Florinel SAVA, Mihai POPESCU

National Institute R&D of Materials Physics, 077125-Bucharest-Magurele, PO Box Mg. 7, Romania
Corresponding author: Florinel SAVA, e-mail: fsava@infim.ro.

The structure of nano-carbon objects (ball-like, nanotubes, defected graphenes) has been modeled by a Monte-Carlo computer procedure. The structure of nano-chalcogenides objects based on two-dimensional network of arsenic sulphide has been modeled. The results were compared to the experimental data whenever possible. The structural modelling was proved as a powerful method for predicting new nano-structural elements in various low-dimensional materials.

Key words: nanocarbon; graphene; chalcogenide; modelling

1. INTRODUCTION

In spite of the enormous progress in synthesis techniques for fullerenes, nanotubes and other nano-carbon objects, the theoretical understanding of their formation and growth lags behind. Graphene separation and investigation is a very recent challenge in nano-physics. Graphene is a one atom thick crystal layer, a chemically stable, electrically conducting membrane exhibiting a variety of unique properties due to its novel molecular structure [1]. The problem of formation and growth of nano-configurations of other low-dimensional materials, as e.g. chalcogenides is still in its infancy. Fullerenes were discovered in 1985 [2], nanotubes in 1991 [3] and hints on the existence of nano-chalcogenides (As_2S_3 nanotubes) only recently [4]. The presently available simulation techniques (semi-empirical, ab-initio and others) are able to provide quantitative understanding of the formation and particularities of the structures as a function of the arrangement of atoms. A microscopic insight into various nano-objects will allow for understanding of the essential physics of the nanomaterials and will open the way towards various applications.

In this paper we used the Monte-Carlo method for modelling new nano-carbon configurations and nano-chalcogenide configurations based on the arsenic sulphide chalcogenide. The final purpose was to predict new configurations in nanomaterials, not yet proved experimentally.

2. MODELLING METHODS

The modelling supposes a procedure for building rational structural models based on calculations consisting in finding the structure of minimum free energy and on inter-atomic interactions chosen according to the crystallo-chemistry principles.

Three main methods are well-known:

- molecular dynamics (MD)
- Monte-Carlo Metropolis (MCM)
- Reverse Monte-Carlo method (RMC).

The molecular dynamics is a simulation method which allows to predict the time evolution of a system with interacting particles and to estimate its relevant physical properties. Thus, the positions and velocity of the atoms (particles) as well as the forces acting upon them at every time can be known exactly. The particle trajectories are calculated by resolving the motion equations for equilibrium and non-equilibrium situations. By using the statistical mechanics are calculated the macroscopic properties of the system as a function of

time: pressure, energy caloric parameters... [5, 6]. The method permits the simulation of time-dependent phenomena: transport phenomena, growth processes, etc.

The method consists in several steps:

- choosing of an initial set of parameters (initial positions and velocities of all the particles of the system)
- choosing the interaction potentials that govern the system and allow for the calculation of the forces acting between the particles
- finding the evolution in time of the system by resolving the classical Newtonian equations for all the particles. The equations are expressed as:

$$\vec{F}_i(t) = m_i \frac{d^2 \vec{r}_i}{dt^2} \quad (1)$$

where F is the force that acts on the particle i at time t and is equal to the negative gradient of the interaction potential U , m_i is the atomic mass and r_i is the position of the particle.

The interaction potentials determine the force field in the system. This force field can be obtained by quantum methods (e.g ab-initio method, by using the Schrödinger equation), by empirical methods (Lennard-Jones [7], Morse [8], Born-Mayer [9]) or quantum empirical methods (embedded atom model [10], glue model [11], bond-order potential [12]). The criteria for selecting the force-field are the accuracy, transferability and calculation speed. A typical interaction potential could consist of a number of bonding interaction terms (potential for bond stretching, bond bending and bond torsion) and non-bonding interactions (van der Waals, electrostatic).

The method has been improved by using the density functional theory (DFT) which leads to more precise geometry and energies. The MD method that uses DFT (first principles) is successful in the study of the dynamical processes but requires huge amounts of computing resources.

The Monte-Carlo-Metropolis method has the following characteristics:

- the problem is treated in an analogous-probabilistic or statistical model.
- the probabilistic model is resolved by a numerical stochastic experiment. In a stochastic process there is not a unique possibility of evolution in time of the processes, as is the case when differential equations are used. Oppositely, there exists some uncertainty regarding the evolution described by the distribution probability. This means that, notwithstanding the knowledge of the initial conditions there exists more possibilities to continue the process, some ways being more probable than others.
- the data are analyzed by using statistical methods.

The simplest procedure is the static Monte-Carlo one. In this method the atoms trajectories are generated by random shifting in space, which leads, step by step, to the minimization of the free energy of the system. This method does not permit the investigation of the processes at the time scale. Temperature is not a variable parameter and the system is, therefore, considered at $T = 0$ K. To accelerate the finding of the minimum energy configuration is better to choose firstly a set of initial coordinates.

The reverse Monte-Carlo method proceeds with the following steps:

- An initial configuration of points (atoms) are admitted (e.g. a set of N points within a cube of side L). It is possible to use random three-dimensional configuration, a special network or a set of coordinates from previous simulations.
- boundary periodical conditions are applied (e.g. the cube is surrounded by its image) and one computes the pair distribution function (PDF, or radial distribution function (RDF)): $g_s(r)$.
- a new configuration is generated by moving randomly one or more points (atoms). A new PDF (RDF) is calculated: $g_s'(r)$.
- the two PDFs, old and new one, are compared with the experimental $g_{exp}(r)$ for the system under investigation by using Pearson test (χ^2 criterion) or least mean square estimation of the difference between the two functions:

$$\chi^2 = \frac{\sum_{i=1}^{n_r} (g_{\text{exp}}(r_i) - g_S(r_i))^2}{\sigma_E^2(r_i)}; \quad \chi'^2 = \frac{\sum_{i=1}^{n_r} (g_{\text{exp}}(r_i) - g'_S(r_i))^2}{\sigma_E^2(r_i)} \quad (2)$$

where n_r is the number of points r_i and σ_E is the experimental error.

- if $\chi' < \chi$ the new configuration is accepted. If $\chi' > \chi$ the new configuration is accepted with a probability that follows a normal distribution, with width σ .

- if the new configuration is accepted, then this one is taken as initial configuration for the next iterative step.

The procedure is repeated till the χ^2 decreases down to the equilibrium value and oscillates around this value as in the case of the energy in the conventional Monte-Carlo method.

3. MODELLING OF NANO-CARBONS

The structural modeling of nano-materials is used not only to understand the structure of the already found materials but also for imagining new atomic configurations, thus predicting new materials. The modeling can also play an important role in the prediction of new properties and can be a guide for the synthesis experiments.

The fullerene C_{60} is condensed on the basis of dispersion forces and is semiconductor. The way of formation of fullerene C_{60} , the most abundant fullerene, has been studied in [13]. There was proposed the “way of reaction of C_{10} rings”. The fullerene is formed with the help of the C_{10} rings. This is because the C_{10} rings are very abundant in ashes and the calculations show that the bonding energy per atom is 0.4 eV/atom, higher than that in the C_{10} chain and this difference is the highest in the series of the investigated clusters C_n ($5 < n < 17$), at the temperature of 2000 K. It was simulated the reaction between two C_{10} rings where the carbon atoms are sp hybridized (Fig. 1), as well as the reaction between a planar cluster and a ring (Fig. 2).



Fig. 1. Instantaneous configuration of the reaction process $C_{10} + C_{10}$ ($T=1500$ K) The two rings knock and thereafter aggregate into a planar C_{20} molecule where the carbon atoms exhibit sp^2 hybridization. The blue and yellow spheres illustrate the atoms that initially formed the two C_{10} rings; finally they mix together.

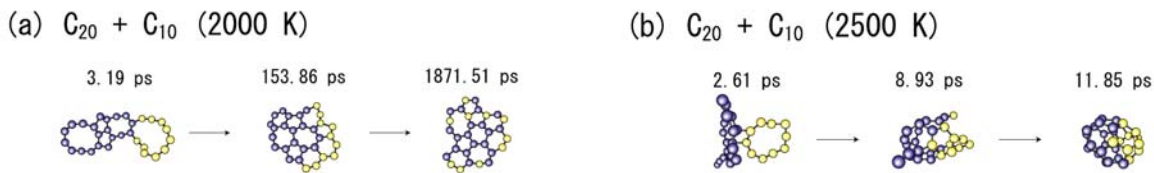


Fig. 2. Instantaneous configurations of the reaction processes of C_{20} and C_{10} (a) at $T=2000$ K and (b) at $T=2500$ K (C_{20} is yellow, C_{10} is blue). In (a) the plane C_{30} consists of sp^2 hybridized orbitals made of hexagons and heptagons. In the reaction (b) the fullerene C_{30} is formed (sp^2 hybridization).

The conclusion was that there are several stages in the formation of a fullerene cluster and the simulation proved that in general the fullerenes are not ideally spherical but strongly asymmetric due to numerous defected embedded in the structure during formation.

In the paper [14] was simulated the growth of the nanostructures in a carbon plasma by using the tight binding molecular dynamics at the scale of nanoseconds (Fig. 3). The simulation shows that clusters of carbons are produced with sp - sp^2 hybridizations of chains, rings and fullerenes, as a function of temperature and atom density.

P.L. de Andres et al. [15] have shown that two superposed graphenes (packing AA) forms a strong chemical bond when the distance between the graphite planes is 1.56 \AA (Fig. 4). In the same time the C-C bonds from every plane are considerably weakened from a partially double bond, 1.41 \AA , to the single bond, 1.54 \AA . This structure is metastable, with an activation energy per cell of 0.16 eV higher than the standard configuration where the bonding is made through Van der Waals forces and the distance between planes is higher (3.35 \AA). The calculations are made in the frame of the DFT theory.

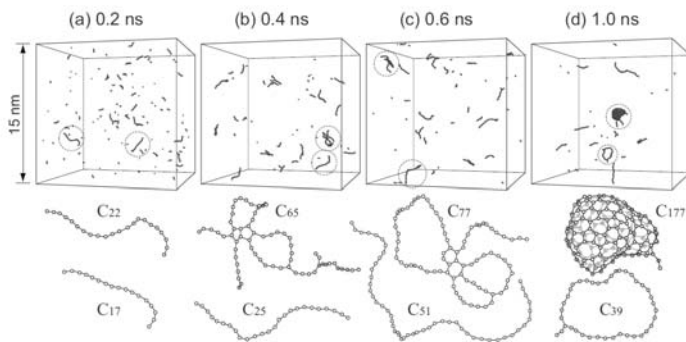


Fig. 3 The simulated growing process of the carbon clusters. Initially 400 atoms are distributed randomly in a cube with the volume of 15 nm^3 at 2000 K . When the interatomic distance is under 1.8 \AA a bond represented by a continuous line is formed.

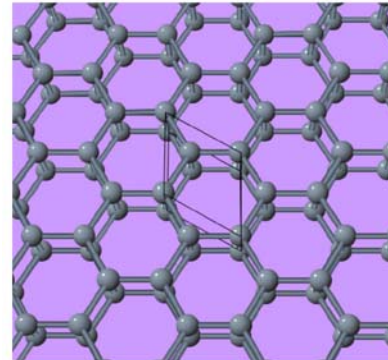


Fig. 4 A metastable two-dimensional structure made of two graphenes with exactly superposed atoms. It is shown the elementary cell: $a=b=2.67 \text{ \AA}$; $\gamma=120^\circ$.

Brey and Palacios [16] have studied the waved graphene, because the transmission electron microscopy experiments have shown that the suspended graphene sheet is not perfectly plane but shows irregularities or waving at the nanometer scale.

Finally we must remark that the inclusion of five-fold rings or seven-fold rings into the growing nanotubes determines the changing in the spatial evolution of graphenes during growth. Charlier and Iijima [17] developed a model and demonstrated on its basis that protrusions in the graphene sheet with a diameter small compared to their height can lead to nanotube nucleation while wider protrusions lead only to strained graphene sheets and no nanotube growth.

We have modelled several special configurations including the attachment of a fullerene molecule to the wall of a nanotube and the coupling of two nanotubes linked perpendicularly. We tried to demonstrate that such configurations are possible from the crystallo-chemistry point of view. We applied the standard Monte-Carlo static procedure using valence force field theory [18] with the force constants reported recently for fullerene C_{60} configuration [19].

Figure 5 and 6 show the final configurations after energy relaxation of the initial models (fullerene + nanotube and nanotube + nanotube) built by hand and whose atomic coordinates were measured directly on the model.

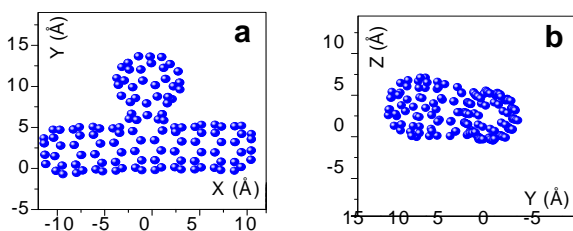


Fig. 5 The configuration with one fullerene molecule (C_{60}) coupled to a nanotube.
Free energy / (bond and angle) = 2.99 meV .

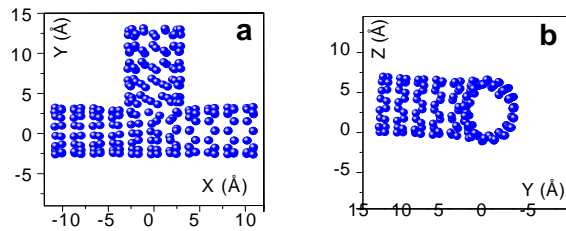


Fig. 6 The configuration with two nanotubes coupled perpendicularly. Free energy / (bond and angle) = 0.682 meV

The results allow to conclude that the change in the free energy during the attachment of the fullerene to nanotube and the coupling of two (open) nanotubes is enough small to guarantee high stability to the complex configurations. In the same time the modeling suggest one new mechanism for the formation of fullerene: the nucleation at the nanotube wall. This is achieved with the help of pentagonal rings accidentally introduced during growth. Another result is the possibility to grow new nanotubes directly on the external

part of a nanotube wall by protruding the wall with the help of hexagonal rings of atoms. Last but not least, we must remark a special aspect of the growth of nanotubes one perpendicular to another: the nanotube, which nucleate on another nanotube at right angle becomes curved, elliptical in cross-section and twisted.

Further, we have modelled the structure of a defected graphene in different cases.

We have grown graphenes starting from one, two or more clustered pentagonal rings, which act as seeds. The growth continues with hexagonal ring, the basic unit of an ideal graphene.

The relaxed structures are very different and demonstrate that the configurations with embedded pentagonal rings shows the tendency to make curved graphenes, to make tubes and even to make fullerenes of different size. It was concluded that the main mechanism of graphene developing by including defects is general and can be put at the basis of the formation of various type of nano-carbon objects. The presence of heptagonal or higher order rings in the centre of a developing graphene leads to the waving of the graphenes. The random distribution of the defects in graphene determines the growth of crystals made of defected graphenes with irregular surface as a function of the type and distribution of the defects. This aspect was confirmed by simulation: freely suspended graphenes are partially crumpled due to bond bending instability [20].

We have simulated the simple graphene structure, with various defects embedded in it, and the results are shown in Fig. 7.

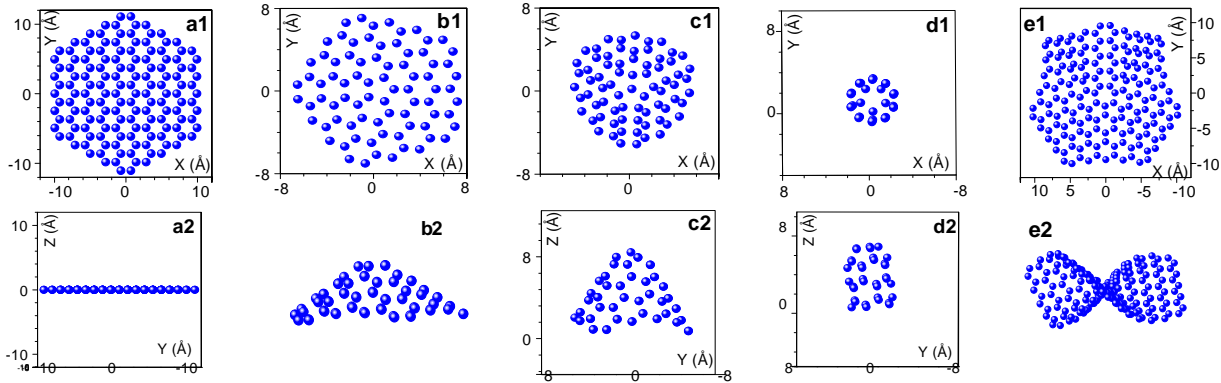


Fig. 7. Various nanoconfigurations obtained from defected graphenes:

- a. ideal grapheme (150 atoms), free energy / (bond and angle) = $3.142 \cdot 10^{-8}$ meV;
- b. one pentagonal ring in the middle of a grapheme (80 atoms), free energy / (bond and angle) = 0.332 meV;
- c. 3 pentagons in grapheme (73 atoms), free energy / (bond and angle) = 1.1 meV;
- d. 6 pentagons in grapheme (35 atoms), free energy / (bond and angle) = 4.79 meV,
- e. one heptagon in grapheme (175 atoms), free energy / (bond and angle) = 0.0152 meV.

An other structure, not yet evidenced experimentally is the nano-torus structure. Nano-tori can be built in the frame of nanotube configurations with open ends. A certain minimum length of a nanotube is necessary in order to close the nanotube. In our simulation the minimum number of unit length was 5. In order to curve the tube, hexagons and heptagons were introduced during nanotube construction, face to face (Fig. 8). If the surface of the nano-torus is developed one can see that the torus formation is possible by the alignment of heptagonal rings embedded in the graphene. The graphene will be distorted out of its plane and will converge to link both sides along the line of heptagons, thus developing the torus-type configuration.



Fig. 8 Toroid-like carbon configuration (240 atoms).

Of course, many other configurations can be built according to the distribution of defects in the graphene sheet. The conclusion is that the ordering of the defects in graphenes can explain the formation of many configurations based on carbon.

4. MODELLING OF THE STRUCTURE OF NANOCHALCOGENIDES

Chalcogenides are a class of compounds and alloys based on the combination of a chalcogen element (sulphur, selenium or tellurium) with other elements (arsenic, phosphorous, germanium, silicon, tin, etc.). One of the typical materials, very stable in the non-crystalline, glassy state is arsenic sulphide (As_2S_3). Because arsenic exhibits the valence three and sulphur valence two, the structure is made of layers consisting in interconnected As_2S_3 pyramids. Taking into account the similarity between carbon (valence three and two-dimensional structure of graphite layers) and As_2S_3 (that forms easily layers of arsenic (valence three) linked to sulfur (valence two)), it was logical to suppose that specific nano-objects based on layers could be obtained.

We have found that only configurations with a strictly determined number of atoms are possible.

We have modelled small clusters, i.e. closed configurations of different sizes, with spherical symmetry and with the same number of atoms in every ring. It was demonstrated that only three different clusters are possible. One As_4S_6 cluster with four 6-fold rings of atoms (free energy / atom = 0.924 meV), one As_8S_{12} , cluster with six eight-fold rings (free energy / atom = 0.0007 meV), and one $\text{As}_{20}\text{S}_{30}$ cluster with twelve ten-fold rings of atoms (free energy / atom = 0.0004 meV).

Trying to build a cluster with only 12 atoms rings (similar to the configuration specific to crystalline orpiment) failed. In all the cases we have considered only heteropolar bonds (As-S) in the structure. The coupling between the upper part of a cluster consisting of a 12-fold rings surrounded by six 12-fold atoms rings was possible only by sulphur bridges, which give rise to 8-fold and 12-fold rings. This cluster, $\text{As}_{48}\text{S}_{72}$, is the second one in the family of clusters with different spatial extension, having the total number of atoms, $N = 30n^2$, with $n = 1, 2, 3, \dots$ (Fig. 9a, b, c)

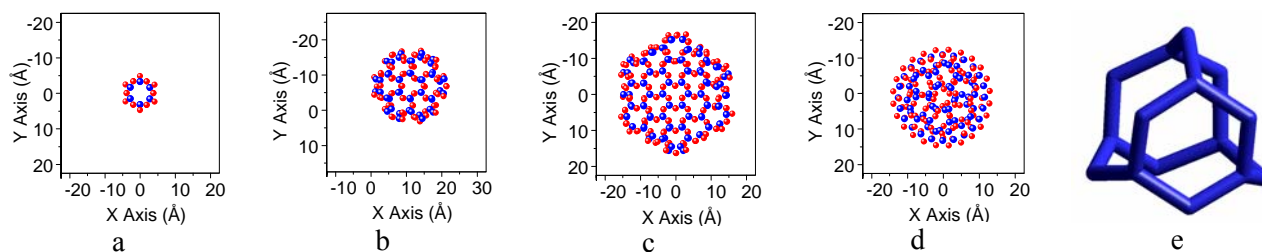


Fig. 9. a. The small nano-pie cluster ($\text{As}_{12}\text{S}_{18}$) $n=1$, free energy / atom = 1.585 meV;
 b. The medium nano-pie cluster ($\text{As}_{48}\text{S}_{72}$) $n=2$, free energy / atom = 1.606 meV;
 c. The large nano-pie ($\text{As}_{108}\text{S}_{162}$) $n=3$, free energy / atom = 0.189 meV;
 d. The medium nano-pie cluster, second family of clusters ($\text{As}_{72}\text{S}_{108}$) $n=2$, free energy / atom = 0.119 meV
 e. The small fullerene-like cluster (As_6S_9), free energy / atom = 0.724 meV;

We reveals a new family of clusters made of two parallel planes of atoms, every layer consisting of a hexagonal packing of As-S, with N atoms in the cluster sequence: $N = 30n(n+1)$ ($n = 1, 2, 3, \dots$). In this family of clusters the linking between planes at boundaries are characterized by alternated 10-fold and 12-fold rings of atoms. Fig. 9d shows the second cluster, $\text{As}_{72}\text{S}_{108}$, for $n=2$.

The shape of the arsenic sulphide clusters, based on twelve-fold As-S rings, approaches that of a pie. We called these clusters nano-pie clusters.

Another family of clusters is fullerene-like clusters. The small fullerene-like cluster is As_6S_9 (Fig 9e), consisting of two six-fold rings and three eight-fold rings. The next cluster is $\text{As}_{16}\text{S}_{24}$, consisting of two eight-fold rings and eight ten-fold rings. The cluster similar with carbon fullerene C_{60} is $\text{As}_{60}\text{S}_{90}$.

We have found that chalcogenide nanotubes can be also obtained. Fig. 10 shows an open nanotube and a closed nanotube.

After finishing the modelling calculation we found in the literature a short report on the formation of nanotubes of around 100 nanometers in diameter [4] by an exotic way: the growth of nanotubes from

solution assisted by microorganisms (*Shewanella* sp. strain HN-41). The image obtained by SEM is shown in Fig. 11. This seems to be a good confirmation of the possibility to get nano-chalcogenides tubes, similar to those existing among the large category of carbon configurations.

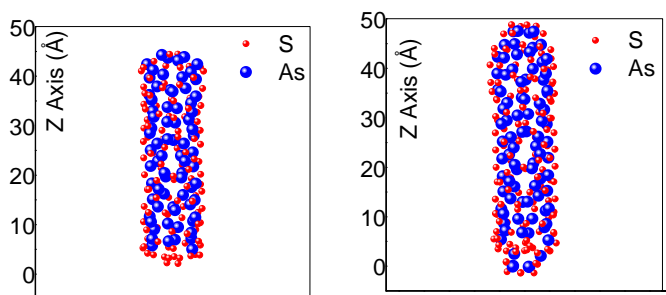


Fig. 10 a. open end nanotube made of As_2S_3 (194 atoms), free energy / atom = 0.004 meV
b. closed end nanotube made of As_2S_3 (230 atoms), free energy / atom = 0.168 meV.

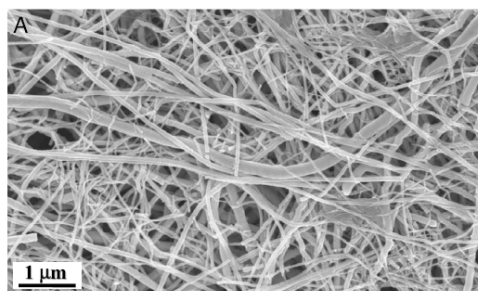


Fig. 11. SEM picture of As-S nanotubes produced with *Shewanella* bacteria.

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REFERENCES

1. K. S. NOVOSELOV, A. K. GEIM, S. V. MOROZOV, D. JIANG, Y. ZHANG, S. V. DUBONOS, I. V. GRIGORIEVA, A. A. FIRSOV, *Science*, **306** (5696), 666-669 (2004).
2. H. W. KROTO, J. R. HEATH, S. C. O'BRIEN, R. F. CURL, R. E. SMALLEY, *Nature*, **318**, 162 (1985)
3. S. IIJIMA, *Nature*, **354**, 56, 55 (1991).
4. JI-HOON LEE, MIN-GYU KIM, BONGYOUNG YOO, NOSANG V. MYUNG, JONGSUN MAENG, TAKHEE LEE, ALICE C. DOHNALKOVA, JAMES K. FREDRICKSON, MICHAEL J. SADOWSKI, HOR-GIL HUR, *Proc. of the National Academy of Sciences of USA*, 18 Dec. 2007, vol. **104**, no. 51, pp. 20410-20415.
5. Q. D. ZHENG, A. B. YU, G. Q. LU, *Progr. Polymer Sci.* **33** (2008), 191-269.
6. T. E. KARAKASIDIS, C. A. CHARITIDIS, *Materials Science and Engineering*, **C27** (2007) 1082-1089.
7. LENNARD-JONES, J. E. COHESION, *Proc. Phys. Soc.* **43**, 461-482 (1931).
8. P. M. MORSE, *Phys. Rev.* **34**, 57-64 (1929).
9. A. A. ABRAHAMSON, *Phys. Rev.* **178**, 76-79 (1969).
10. DAVY MURRAY S., MIKE BASKES, *Phys. Rev.* **29**(12), 6443-6453 (1984).
11. B. K. GODWAL, R. S. RAO, R. CHIDAMBARAM, *J. Non-Cryst. Solids*, **334-335**, 117-120 (2004).
12. L. PAULING, *The Nature of the Chemical Bond*, 3-rd ed., Cornell University Press, Ithaca NY, 1960.
13. Y. UENO, S. SAITO, *Physical Review B* **77**, 085403 (2008).
14. Y. YAMAGUKI, L. COLOMBO, P. PISERI, L. RAVAGNAN, P. MILANI, *Physical Review B* **76**, 035405 (2008).
15. P. L. DE ANDRES, R. RAMIREZ, J. A. VERGES, *Phys. Rev. B* **77**, 045403, 2008.
16. BREY, J. J. PALACIOS, *Phys. Rev. B* **77**, 041403 (2008).
17. JEAN-CHRISTOPHE CHARLIER, SUMIO IIJIMA, "*Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*" Series: Topics in Applied Physics, Vol. 80, Dresselhaus, Mildred S.; Dresselhaus, Gene; Avouris, Phaedon (Eds.) 2001, pp. 55-81.
18. P. N. KEATING, *Phys. Rev.* **145**, (1966) 637.
19. R. A. JISHI, R. M. MIRIE, M.S. DRESSELHAUS, *Phys. Rev. B* vol. **45**, no. 23, 13685-13689, 1992.
20. J. C. MEYER, A. K. GEIM, M. I. KATSNELSON, K. S. NOVOSELOV, T. J. BOOTH, S. ROTH, *Nature*, **466**, 60 (2007).

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