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Polymerization of miniature fullerenes in the cavity of nanotubes

O. E. Glukhova · A. S. Kolesnikova · M. M. Slepchenkov

Abstract The polymerization of four fullerenes C_{28} in the cavity of closed single-walled carbon nanotube C_{740} was investigated. It was shown that the formation of the oligomer of four C_{28} fullerenes is observed at the pressure of 37.73 GPa, which is created by means of the charged fullerene C_{60}. Fullerene C_{60} moves under the influence of an external electric field.

Keywords Carbon nanotube · Nanopeapod · Polymerization · Pressure

Introduction

The boundaries of application for carbon nanotubes depend largely on the ability to modify their intrinsic properties by manipulating their structure. Therefore, the search of new structural modifications of carbon nanotubes and their practical application are the subject of many scientific research works.

One of the most effective ways to modify the properties of carbon nanotubes is the filling of its interior cavity with other molecules. In particular, the fullerene molecules can be used as such molecules. First, the model of single-walled carbon nanotube filled with one-dimensional chains of C_{60} fullerenes was proposed in the work [1]. The structures formed as a result of the fullerenes encapsulation in a carbon nanotube were called "peapods". Several technologies of the peapods synthesis exist. For example, the synthesizing process of these structures can be manufactured via a vapor phase or surface diffusion mechanism [2]. Synthesis of peapods can be performed on silicon substrates. In particular, this technology of

synthesis has been used for the synthesis of single-walled carbon nanotubes (SWNTs) filled with C_{60} and for the synthesis of metallo-fullerenes Gd@C_{82} [3]. The proposed synthesis procedure involves the following steps: 1) catalytic metal deposition on a SiO2/Si substrate; 2) thermal chemical vapor deposition of pod SWNTs; 3) cap opening of the pod SWNTs by means of the annealing in dry air; 4) doping of pea fullerenes in vapor phase.

Process of the fullerenes encapsulation can occur in the cavity of double-walled carbon nanotubes (DWNTs). Double-wall carbon nanotubes encapsulating C_{60} and C_{70} fullerenes have been synthesized by the vapor reaction method [4]. Annealed DWNTs with pure fullerenes (99.9 %) were sealed in an H-shape glass tube under a pressure of $1 \cdot 10^{-5}$ Torr and heated at 500 °C for 48 h. Further, washing with CS_2 solvent was performed to remove C_{70} fullerenes adhering to the outer wall of DWNTs. Then, the solution CS_2 was removed by heat treatment at 300 °C. The filling of single wall carbon nanotubes with fullerenes from solvent can occur at low temperatures (below 69 °C). In particulary, it was shown that a 2-hour long refluxing in N-hexane of the mixture of the fullerene and SWCNT results in a high yield of $C_{60}(C_{70})$@SWCNT peapod [5]. Another synthesis method of the peapod is the introduction of the fullerene molecules into tubes by heating fullerene powders with SWNTs in a sealed quartz tube [6].

Peapods have a number of interesting physical properties. It was established that an effect of polymerization of the encapsulated fullerenes occurs inside peapod due to the external pressure [7–9]. Peapods obtained by heating mixture (CNT and C_{60}) in a sealed quartz cell were placed in a solution of methyl and ethyl alcohol. Further the processing of mixture by means of the pressure with a diamond anvil was held. As a result of the X-ray diffractometric measurements it was revealed the average distance between the molecules C_{60} inside peapod decrease from 1 to 0.85 nm

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when the pressure is of the order 2 GPa. This result corresponds to the distance between the surfaces of neighboring fullerene molecules (~ 0.145 nm), which is comparable with the distance between neighboring carbon atoms in the fullerene molecule. This fact indicates the presence of the polymerization effect for C_{60} inside peapod.

The possibility of the polymerization of C_{28} inside the tube have practically not been investigated, although it is known that the C_{28} is easy from the polymers [10, 11]. This process occurs because of the four sp^3-hybridized atoms located in the top of tetrahedron underlying in a basis of symmetry of the atomic framework.

The aim of this paper is the study of the polymerization process of four fullerenes C_{28} in the cavity of closed single-walled carbon nanotube C_{740}. Simulation of the polymerization process was carried out using the model of the nanoautoclave device. Model of the nanoautoclave is presented in work [12].

Computational methods

In this work, the molecular dynamics (MD) method and tight binding (TB) method were applied to calculate the location of the shuttle-molecule in the nanotube and its movement. To calculate the interaction energy between bonded atoms of the nanotubes and the fullerene the tight binding method is used. Within the TB method [12] the total energy of a system of ion cores and valence electrons is written as:

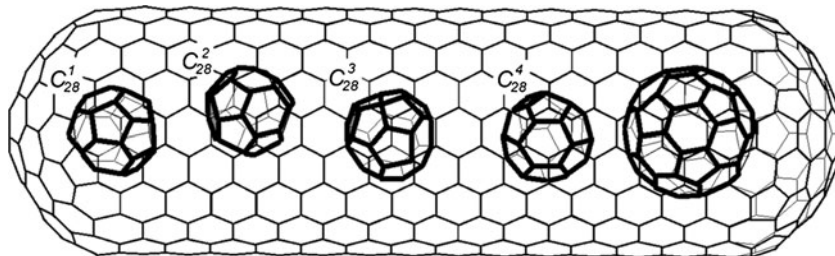$$E_{tot} = E_{bond} + E_{rep} + E_{vdW} \qquad (1)$$

Here the term E_{bond} is the bond structure energy that is calculated as the sum of energies of the single-particle occupied states. Those single-particle energies are defined by solving the Schrodinger equation

$$\widehat{\mathbf{H}}|\psi_n\rangle = \varepsilon_n|\psi_n\rangle, \qquad (2)$$

where $\widehat{\mathbf{H}}$ is the one-electron Hamiltonian, ε_n is the energy of the nth single-particle state. The wave functions $|\psi_n\rangle$ can be approximated by linear combination

$$|\psi_n\rangle = \sum_{l\alpha} C_{l\alpha}^n |\varphi_{l\alpha}\rangle, \qquad (3)$$

where $\{\varphi_{n\alpha}\}$ is an orthogonal basis set, l is the quantum number index and α labels the ions. The matrix elements in Eq. (2) are calculated after fitting a suitable database obtained from the experiments. The results of the experiments were presented in [13].

Term E_{rep} in Eq. (1) is the phenomenological energy that is the repulsive potential. It can be expressed as a sum of two-body potentials

$$E_{rep} = \sum_{\alpha,\beta\rangle\alpha} V_{rep}(r_{\alpha\beta}), \qquad (4)$$

where V_{rep} is a pair potential between the atoms at α and β. This two-body potential describes an interaction between bonded and nonbonded atoms and it is written as: [13]

$$V_{rep} = V_{ij\gamma}^0 \left(\frac{1.54}{r_{\alpha\beta}}\right)^{2.796} \exp\left\{2.796\left[-\left(\frac{r_{\alpha\beta}}{2.32}\right)^{22} + \left(\frac{1.54}{2.32}\right)^{22}\right]\right\}, \qquad (5)$$

where i and j are orbital moments of wave function, γ presents the bond type (σ or π). The values of the parameters $V_{ij\gamma}^0$ are: $V_{ss\sigma}^0 = -4.344, V_{sp\sigma}^0 = 3.969, V_{pp\sigma}^0 = 5.457, V_{pp\pi}^0 = -1.938$ eV.

To describe the intermolecular interaction the van der Waals potential was added to the system energy (1). The van der Waals potential is given as the Lennard-Jones potential [14]:

$$E_{vdW} = \sum_{\alpha,\beta\rangle\alpha} \frac{A}{\sigma^6}\left(\frac{1}{2}y_0^6 \frac{1}{(r_{\alpha\beta}/\sigma)^{12}} - \frac{1}{(r_{\alpha\beta}/\sigma)^6}\right), \qquad (6)$$

where $\sigma=1.42$ is the length of the C-C bond, $y_0=2.7$ and $A=24.3 \ 10^{-79}$J m^6 are empirically chosen parameters [14]. However, the Lennard-Jones potential is incorporated only if the phenomenological intermolecular energy becomes zero (at the distance of about 0.25 nm for the carbon-carbon interaction).

The motions of the atoms are determined by the classical MD method where Newton's equations of motion are integrated with a third-order Nordsieck predictor corrector [15]. Time steps of 0.15–0.25 fs were used in the simulations. The forces on the atoms were calculated using TB method.

Fig. 1 Location of fullerenes in a capsule C_{740} in the original equilibrium state of the system

Table 1 Some parameters characterizing interaction of fullerene C_{60} with fullerenes C_{28}, leading to the dimer formation

h,Å	D,Å $C_{28}^4 - C_{60}$	D,Å $C_{28}^2 - C_{28}^1$	D,Å $C_{28}^3 - C_{28}^2$	D,Å $C_{28}^4 - C_{28}^3$	E_{inter}, eV C_{28}^1	E_{inter}, eV C_{28}^2	E_{inter}, eV C_{28}^3	E_{inter}, eV C_{28}^4
5.5	2.73	2.49	2.49	2.64	−1.01	−0.81	−0.84	−0.87
6	2.6	2.58	2.4	2.76	−1.02	−0.81	−0.83	−0.86
6.5	2.43	2.6	2.2	2.5	−1.02	−0.71	−0.69	−0.81
7	2.36	2.54	2.23	2.32	−1.016	−0.45	−0.32	−0.66
7.5	2.23	2.38	2.07	2.5	−0.93	1.56	1.88	−0.12
8	2.25	2.21	2.02	2.35	−0.48	2.69	2.97	1.75
8.5	2.078	2.05	1.94	2.11	1.82	6.32	9.39	7.31

Simulation the polymerization process of fullerenes C_{28} inside nanotube C_{740}

The enthalpy of the $C_{60}+tubeC_{740}\rightarrow C_{60}@C_{740}$ reaction was calculated by means of the tight-binding method. It is exothermal and the enthalpy is equal to -50.22 kcal mol^{-1}. The enthalpy of the $4C_{28}+tubeC_{740}\rightarrow 4C_{28}@C_{740}$ reaction is equal to -111.2 kcal mol^{-1}. Therefore, such configurations $4C_{28}@C_{740}$ and $C_{60}@C_{740}$ are energetically favorable.

In the initial state of the system the positively charged molecule C_{60} with a diameter of 6.7 Å is positioned in one of the potential wells, which are located on both ends of nanocapsule. Closed with both sides nanotube C_{740} is a nanocapsule (Fig. 1). The diameter of the nanotube C_{740} is equal to 13.53 Å. The length of the nanotube C_{740} is equal to 44.14 Å. Four smallest fullerenes C_{28}, with faces facing each other, are located in the opposite potential well of the nanotube. The distance between the molecules of C_{28} is about 3 Å. Fullerene molecule C_{28} belongs to the fullerenes class with tetrahedral symmetry group. The radius of the sphere circumscribed around the fullerene is equal to 2 Å.

Charged fullerene C_{60} in an external electric field starts to move and plays a role of the press. The four molecules of C_{28}

Fig. 2 Stage of the polymerization of fullerene C_{28} under the influence of pressure on them by fullerene C_{60} : **a)** formation of dimer; **b)** formation of trimer; **c)** formation of oligomer
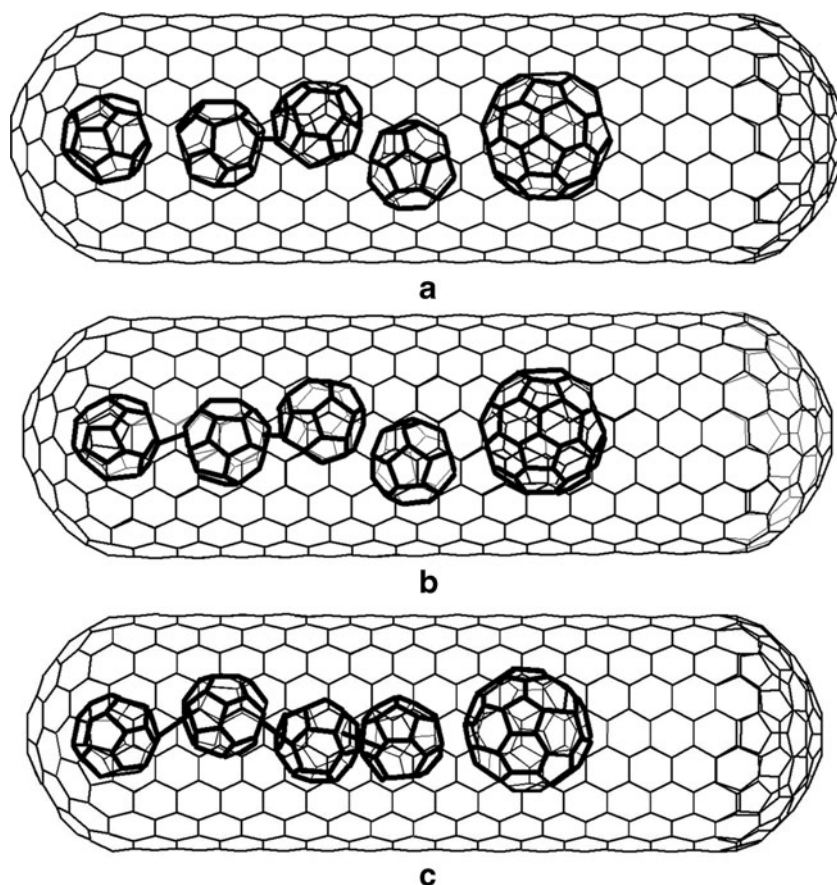
Table 2 Some parameters characterizing interaction of fullerene C_{60} with fullerenes C_{28} leading to the trimer formation

h,Å	D, Å $C_{28}^3 - C_{60}$	D, Å $C_{28}^3 - C_{28}^1$	D,Å $C_{28}^3 - C_{28}^2$	E_{inter},eV C_{28}^1	E_{inter},eV C_{28}^2	E_{inter},eV C_{28}^3
8.8	2.25	2.03	2.46	2.31	2.09	−0.45
9	2.22	2.01	2.39	2.92	3.11	0.13
9.2	2.16	1.95	2.31	5.27	5.80	1.13

are under the pressure by means of the movement of the press along the axis of the capsule to the opposite end. This pressure is caused by the van der Waals interaction of C_{28} fullerenes with C_{60} fullerene and nanotube. Also, fullerene-shuttle can be charged by ion Li encapsulated in the fullerene. Doping of the fullerenes C_{60} by Li atoms is possible. For example, this process can be performed by means of the fullerite C_{60} radiation with a beam of lithium ions with energies of 30 eV [16]. We have established that the fullerene C_{60} with charge of 1e comes out of the potential well at the field strength of 10^7 V/cm. The process of the field emission is occurred at this value of the field strength. Since the nanotube is destroyed due to the field emission the value of the field strength must be reduced. For this purpose the fullerene C_{60} in our simulation has the charge equal to 3e. In our simulation, the field strength at which the fullerene C_{60} comes out of the potential well was equal to 10^5 V/cm.

Orientation of fullerene C_{28} in tube changes at the motion of the molecule C_{60}. Fullerenes C_{28} are shifted closer to the fullerene cap of the tube, slightly moving off from the tube axis, and turning by the sides to each other. Energy of interaction between the fullerenes C_{28} starts to increase with decreasing distance between them. The moment of the electron clouds overlap for fullerenes C_{28} is fixed by means of the increasing of the value for the repulsion energy of the van der Waals interaction E_{rep} electron orbitals [12].

This process within the developed model is a phased process. At the first phase the chemical bond was formed between two central C_{28} fullerenes, close to a distance of 1.94 Å. This distance is necessary for overlap of the π-electron clouds. From Table 1 one can seen that the fullerene C_{60} has moved from its original position on 8.5 Å for the

formation of dimer, and the distance between the fullerene C_{28} located near the fullerene caps and the dimer was equal to 2.05 Å. The distance between the fullerene C_{28} which is located near the molecule of C_{60} and dimer was equal to 2.11 Å (Fig. 2a). In this case the highest values of the van der Waals interaction energy and repulsive energy equal to 9.39 eV and 9.94 eV, respectively, are observed for the third fullerene from the edge of the nanotubes. The pressure which was exerted on the third from the edge of nanotube fullerene C_{28} was equal to 22.18 GPa. In the second phase the fullerene C_{60} has shifted some more on 0.7 Å and the resulting dimer has formed a chemical bond with C_{28} fullerene located near the fullerene caps at the end of the nanotube (Fig. 2b). The distance between the dimer and fullerene C_{28} was equal to 1.95 Å in the moment of the formation of chemical bonds. Form the Table 2 one can see that the resulting trimer and last fullerene C_{28} were located at the distance of 2.31 Å from each other. At the same time, the largest value of the van der Waals interaction energy equal to 5.8 eV and the largest value of repulsive energy equal to 7.06 eV were observed for the dimer, which inter-

Table 3 Some parameters characterizing interaction of fullerene C_{60} with fullerenes C_{28} leading to the oligomer formation

h,Å	D,Å $C_{28}^2 - C_{60}$	D,Å $C_{28}^2 - C_{28}^1$	E_{inter}, eV C_{28}^1	E_{inter}, eV C_{28}^2
9.5	2.25	2.05	6.47	10.34
9.7	2.03	1.98	10.10	15.97

Table 4 Value of repulsive energy on different phases of fullerenes C_{28} polymerization

h,Å	U_{rep}, eV C_{28}^1	U_{rep}, eV C_{28}^2	U_{rep}, eV C_{28}^3	U_{rep}, eV C_{28}^4
Until dimer forming				
5.5	0	0	0	0
6	0	0	0	0
6.5	0	0.09	0.09	0
7	0	0.33	0.40	0.07
7.5	0.05	2.31	2.56	0.58
8	0.48	3.42	3.63	2.32
8.5	2.79	7.02	9.94	7.86
After dimer formation				
8.8	3.27	3.41	0.30	-
9	3.88	4.40	0.86	-
9.2	6.21	7.06	1.78	-
After trimer formation				
9.5	8.52	10.85	-	-
9.7	12.11	16.39	-	-

Table 5 Value of pressure exerted by fullerene C_{60} on fullerenes C_{28} in the process of them polymerization

h,Å	P,GPa C_{28}^1	P,GPa C_{28}^2	P,GPa C_{28}^3	P,GPa C_{28}^4
Until dimer formation				
8.5	4.3	14.9	22.18	17.27
After dimer formation				
9	6.89	7.34	0.3	-
9.2	12.4	13.7	2.6	-
After trimer formation				
9.5	15 .28	24.4	-	-
9.7	23.86	37.73	-	-

acts with two others fullerenes and the tube wall. Dimer has experienced the highest pressure of 13.7 GPa at the moment of the trimer formation. In the final third phase the fullerene C_{60} has shifted some more on 0.5 Å and the resulting trimer has attached the fullerene C_{28} which was nearest to the direction of molecule-shuttle C_{60}. Thus the highest value of the van der Waals interaction energy and repulsive energy were observed at the fullerene C_{28}, which is nearest to fullerene C_{60}. The value of the van der Waals interaction energy was equal to 15.97 eV, and the value of the repulsive energy was equal to 16.39 eV. Fullerene C_{28} nearest to fullerene C_{60} experiences the highest pressure of 37.73 GPa for the formation of the oligomer. All of the above phases of process of fullerenes C_{28} polymerization were presented in Fig. 2.

Value of interaction energy between the polymerizing fullerenes C_{28} and fullerene C_{60}, as well as values of the pressure exerted by a molecule of C_{60} on the miniature fullerenes, are shown in Tables 1, 2, 3, 4 and 5. The step of shift of fullerene C_{60} with respect to the equilibrium position h, inter-cluster distance D, inter-cluster interaction energy E_{inter}, repulsive energy of interaction between fullerenes U_{rep}, pressure P, exerted by fullerene C_{60} on

miniature fullerenes, were presented in Tables 1, 2, 3, 4 and 5.

As a result of simulation of the polymerization process it was established that necessary conditions for the successful completion of the polymerization process of four fullerenes C_{28} inside nanotube C_{740} are as follows: 1) the distance between polymerizable fullerenes C_{28} should be equal to 1.9 Å; 2) the fullerene molecule C_{60} must be displaced from its original position (from a potential well) in the area of the location of the other potential well on 9.7 Å; 3) the pressure exerted by molecule C_{60} on the fullerenes C_{28} should be equal to 37.73 Å. In this paper the pressure is the bulk energy density of the interaction of fullerene C_{28} with surrounding objects: neighboring fullerene C_{28}, nanotube wall and the approaching molecule C_{60}. Chain of fullerenes C_{28} was formed by polymerization process. This chain was presented in Fig. 3.

Chemical bonds formed between the polymerizable fullerenes are retained after the disappearance of the pressure exerted by fullerene C_{60}.

Conclusions

In the course of numerical simulation the theoretical possibility of the polymerization of fullerenes C_{28} inside nanocapsules C_{740} was established. Necessary and sufficient conditions for the formation of the chains of miniature fullerenes C_{28} were formulated as a result of the investigation. It was established that the polymerization of fullerenes C_{28} occurs at the distance of 1.9 Å between them. The formation of the oligomer of four C_{28} fullerenes was observed at a pressure of 37.73 GPa, created by means of the charged fullerene C_{60}, while moving under the influence of an external electric field. Further approach of fullerenes can lead to their deformation. It was found that the chemical bonds formed between C_{28} fullerenes are not after the disappearance

Fig. 3 The chain of fullerenes C_{28} formed as a result of the polymerization process
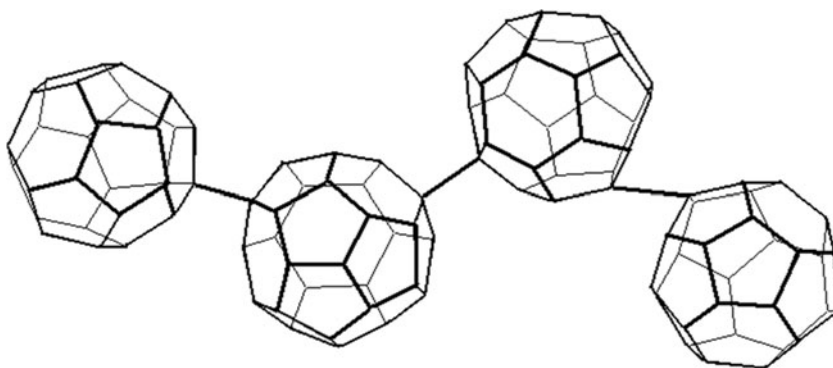
of the pressure on fullerene C_{28}. Consequently, the formation of oligomers in the nanoautoclave is possible.

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