

Dimerization of miniature C₂₀ and C₂₈ fullerenes in nanoautoclave

Olga E. Glukhova

Received: 22 February 2010 / Accepted: 17 May 2010 / Published online: 30 May 2010
© Springer-Verlag 2010

Abstract A mathematical model of the new nanodevice based on the K⁺@C₆₀@tubeC₇₄₀ hybrid carbon compound and named as the nanoautoclave is presented. The operation of the nanoautoclave is demonstrated by the example of modeling the synthesis process of stable dimers of the C₂₀ and C₂₈ fullerenes. Energetic characteristics of the (C₂₀)₂[2 + 2] dimer correspond to those calculated before. Parameters of the (C₂₈)₂[1 + 1] dimer have been calculated for the first time. The dimerization process is simulated by the method of molecular dynamics with the tight-binding description of interatomic interactions.

Keywords Dimerization · Fullerenes · Molecular dynamics · Nanoautoclave · Nanodesign · Nanodevice

Introduction

The discovery of carbon nanotubes in 1991 has stimulated very broad and intensive research into the analyses of their applications [1]. For example, carbon nanotube is applied as nanoreactors. Cobalt ferrite nanowires with an average diameter of 50 nm and lengths up to several micrometers are synthesized inside carbon nanotube [2]. Carbon nanotube may also serve as nanoreactor for a simple thermal reaction process resulting in the fabrication of high-quality, large-yield, single-crystalline Mg₃N₂ nanowires [3].

In this paper, the mathematical model of a new nanodevice—a nanoautoclave, based on a carbon nanotube is presented and validated. The mathematical model of the

nanoautoclave is described and implemented using molecular dynamics (MD) with tight-binding (TB) method to calculate the total system energy. Nanoautoclave work is demonstrated on the example of dimerization reaction of the C₂₀ and C₂₈ fullerenes inside a nanotube under axial compression. Atomic structure and stability of (C₂₀)₂ dimer were studied using TB [4] and density functional theory (DFT) [5]. Geometrical parameters, heat of formation, density of one-electron states for C₂₈ hyperdiamond were determined by using of semi-empirical quantum chemistry PM3-method [6]. However, the process of a dimerization reaction of those fullerenes and its conditions were not researched. As known from [7], in nanotubes such as (10,10), (11,11), and (12,12), C₂₀ and C₂₈ fullerenes form new 1D-, 2D-, and 3D(spiral)- complexes to each other without sealing to the nanotube walls.

Nanoautoclave model

In our nanoautoclave model a closed single-wall carbon nanotube (10,10) C₇₄₀ is represented as a capsule that is closed from both ends with C₂₄₀ fullerene caps. The pressure is controlled by a shuttle-molecule encapsulated into a nanotube that may move inside the tube. In the present case a shuttle-molecule is the C₆₀ fullerene. The shuttle must have some electric charge for its movement to be controlled by an external electric field. The positively charged endohedral complex K⁺@C₆₀ (the ion of potassium inside the fullerene C₆₀) is a shuttle-molecule in the present model of the nanoautoclave. So, the hybrid compound K⁺@C₆₀@tubeC₇₄₀ is a nanoautoclave model. The K⁺@C₆₀@tubeC₇₄₀ nanoparticle is located between two electrodes connected with a power source (see Fig. 1). Changing the potentials at the electrodes, we control the movement of the K⁺@C₆₀ fullerene.

O. E. Glukhova (✉)
Department of Physics, Saratov State University,
410012 Saratov, Russia
e-mail: graphene@yandex.ru

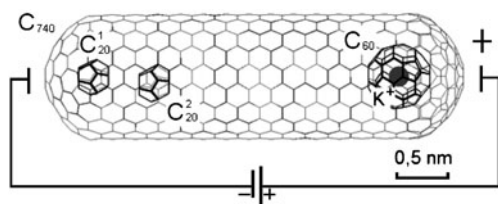


Fig. 1 The nanoautoclave model based on the $K^+@C_{60}@tubeC_{740}$ hybrid carbon compound

Computational method

In this work, the MD and TB 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 TB method is used. The TB method was earlier presented in [8] and to study a stability of carbon nanoclusters was successfully implemented. The total energy of a system of ion cores and valence electrons is written as

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

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 known by solving the Schrödinger equation

$$\hat{H}|\psi_n\rangle = \epsilon_n|\psi_n\rangle, \quad (2)$$

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

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

where $\{\phi_{l\alpha}\}$ 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 and were presented in [8].

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

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

where V_{rep} is pair potential between atoms at α and β . This two-body potential describes an interaction between bonded and nonbonded atoms and is presented in [8]

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

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 [8].

To describe the intermolecular interaction the van der Waals potential was added in to the system energy (1). The van der Waals potential is given as the Lennard-Jones potential [9]:

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

where $\sigma=1.42$ is a length of the C–C bond, $y_0=2.7$ and $A = 24.3 \cdot 10^{-79} J \cdot m^6$ are empirically chosen parameters [9]. However, the Lennard-Jones potential is incorporated only if the phenomenon intermolecular energy becomes zero (at distance 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 [10]. Time steps of 0.15–0.25 fs were used in the simulations. The forces on the atoms were calculated using TB method.

To research the dimerization process in a nanoautoclave our own program was used.

Results and discussion

Using TB the enthalpy of the $C_{60} + tubeC_{740} \rightarrow C_{60}@C_{740}$ reaction was calculated. It is exothermal and the enthalpy is equal -50.22 kcal mol $^{-1}$. At the ground state of the $C_{60}@C_{740}$ hybrid compound the C_{60} fullerene is located at one of the nanotube ends, and the C_{20} or C_{28} fullerenes are located at the opposite end (see Fig. 2a). The shuttle-molecule C_{60} has a distance of about 3.4 Å from the tube walls therefore it may move freely along the nanotube axis under an external electric field. Its atoms are in $sp^{2.28}$ hybridization that makes the fullerene chemically inactive

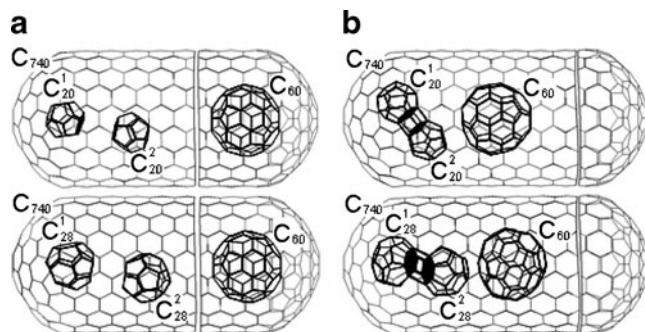


Fig. 2 Stages of dimerization process of the C_{20} and C_{28} fullerenes in the nanoautoclave model: **a** ground state of $K^+@C_{60}@tubeC_{740}$ nanoparticle with the encapsulated fullerenes; **b** $(C_{20})_2[2+2]$ stable dimers and $(C_{28})_2[1+1]$ dimers

Table 1 Characteristics of the interaction between the C₆₀ fullerene and the C_n fullerenes (n=20, 28)

n	d ₁ , Å C _n ² – C ₆₀	d ₂ , Å C _n ² – C _n ¹	R, Å C _n ²	E _a , eV/atom C _n ²	E _{inter} , eV C _n ²	E _{rep} , eV C _n ² – C _n ¹	E _{rep} , eV C _n ² – C ₆₀	P, GPa C _n ²
20	2.65	2.46	2.02	-42.302	1.350	0.00	0.00	6.27
	2.6	2.38	2.01	-42.241	2.557	0.00	0.00	12.42
	2.4	1.95	1.99	-41.916	9.056	0.31	0.15	43.20
28	2.66	2.50	2.78	-42.34	7.20	0.00	0.00	12.8
	2.34	2.33	2.77	-42.05	14.73	0.07	0.06	26.47
	2.33	2.0	2.63	-41.95	16.77	0.20	0.18	35.21

in comparison with the C₂₀ and C₂₈ fullerenes, which have some atoms in sp³ hybridization and will freely polymerize at short distance. The distance between the miniature fullerene and the tube wall is 3.49 Å.

At the start moment, the mutual positions of all nano-autoclave components correspond to the ground state (see Fig. 2a). Creating a certain potential difference at the electrodes, we can stimulate the C₆₀ fullerene movement to the opposite end of the nanotube. The source material for the dimerization (the C_n fullerenes) suffers greater pressure from the shuttle-molecule and the fullerene orientations are changed. They 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. When the pressure created in the tube provides both the overlap of π-electrons of the C_n fullerenes (that corresponds to the interatomic distance of about 1.9 Å) and the covalent bonds formation, the intermediate phase of the (C_n)₂ dimer is synthesized: (C₂₀)₂ [5 + 5] (at n=20) or (C₂₈)₂ [6 + 6] (at n=28). Here and further, a number of fullerene atoms participating in the intermolecular bonds formation is shown in square brackets. Figure 2b shows a stable dimer of the C₂₀ (C₂₈) fullerene and the C₆₀ molecule that suffered a certain deformation.

Table 1 gives the dynamics of some geometrical and energetic characteristics of the C_n fullerenes during the dimer formation process. The following denotations are used: d is the intermolecular distance, R is the fullerene radius, E_a is the energy per atom of the fullerene, E_{inter} is the energy of intermolecular interactions (this energy is the sum of the Lennard-Jones potential and the phenomenon energy), E_{rep} is the phenomenon energy of the fullerenes interaction, P is the pressure (the latest three characteristics will be described below). After returning the C₆₀ molecule

to the start state (in the result of changing the direction of external electrical field strength), the (C_n)₂ dimer is isomerized with the re-orientation in the tube field. So, (C_n)₂ transfers to the stable phase [2+2] n=20 and [1+1] (n=28) (see Fig. 2b).

The characteristics of stable dimers (minimum and maximum lengths of the fullerenes bonds r_{min}/r_{max}, an intermolecular bond length D, a binding energy E_b, an enthalpy ΔH of the isomerization reaction, a band gap E_g and a HOMO (highest occupied molecular orbital) are given in Table 2. A band gap E_g is a HOMO/LUMO gap, where LUMO is the lowest unoccupied molecular orbital.

The structure of stable dimers with the horizontal symmetry plane, symmetry axes, and the plot of electron states density are shown in Fig. 3. The calculated binding energy, band gap of the (C₂₀)₂ dimer well correspond to the data presented in [4], where they are calculated by Hartree-Fock method. The (C₂₈)₂ dimer is studied for the first time.

Modeling the fullerenes dimerization in the nanoautoclave is performed by MD with TB description of the interatomic interaction. Pressure is calculated as a cubic density of the interaction energy between the C_n fullerene and environmental objects: the adjacent C_n fullerene, the walls of the tube-capsule and the shuttle-molecule. The fullerene volume is referred to as a radius R sphere volume holding the fullerene. The overlap moment of electron clouds of the C_n fullerenes is fixed according to the rising value of the intermolecular phenomenon energy E_{rep} of electron orbitals (4).

At the moment of the covalent bonds formation, the pressure is calculated according to the energy E_{inter} = E_{vdW} + E_{rep}. The potential difference at the electrodes Δφ that provides the pressure necessary for the dimerization is calculated according to the relationship ΔE_{inter} = e · Δφ,

Table 2 Characteristics of stable fullerenes dimers

Dimer	Symmetry group of the dimer	r _{min} /r _{max} , Å	D, Å	E _b , eV	ΔH, $\frac{kcal}{mol-atom}$	E _g , eV	HOMO, eV
(C ₂₀) ₂ [2 + 2]	D _{2h}	1.43/1.62	1.65	6.44	-5.01	0.66	7.00
(C ₂₈) ₂ [1 + 1]	C _{2h}	1.41/1.56	1.56	6.57	-2.07	0.14	7.16

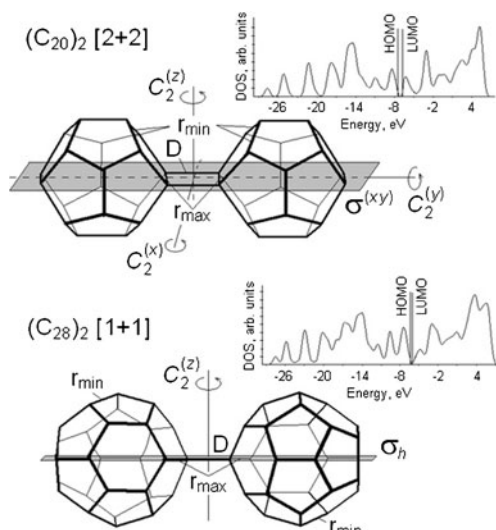


Fig. 3 Stable $(C_{20})_2[2+2]$ dimers and $(C_{28})_2[1+1]$ dimers

where ΔE_{inter} is a potential barrier overcome by the C_{60} fullerene when it goes from the well (the area of the tube end) to the position providing the dimer formation. The strength is calculated as $\Delta\phi/L$, where a distance L is taken to be equal to the capsule length added to value of 3.4 \AA (closing the capsule to electrodes by a less distance may cause sticking due to van der Waals interaction). The C_{740} capsule length is equal to 44.56 \AA . In spite of the significant value, the strength is not critical for the nanotube and is quite achievable. It is known that the electron autoemission is observed at $F = 10^9 \div 10^{10} \text{ V/m}$. Table 3 presents the potential barrier ΔE_{inter} for the C_{60} fullerene, the C_{60} fullerene energy $E_{\text{inter}}(1)$ in the potential well, the potential

Table 3 The energy of the C_{60} fullerene and parameters of the outer field necessary for the $(C_n)_2$ dimer synthesis

$(C_n)_2$	$E_{\text{inter}}(1)$, eV	ΔE_{inter} , eV	$\Delta\phi$, V	F, V/m
$(C_{20})_2[2+2]$	-3.574	5.42	8.90	$0.18 \cdot 10^8$
$(C_{28})_2[1+1]$	-3.574	6.50	10.16	$2 \cdot 10^8$

difference $\Delta\phi$, and the external field strength F necessary for dimer formation.

In conclusion, the dimer synthesis in nanoautoclave is real (the energetic parameters of the C_{20} fullerene dimer correspond to those calculated before), the $(C_{28})_2[1+1]$ dimer is stable and may be synthesized in the field of the nanotube holding potential. Finally, the compound $K^+@C_{60}@tubeC_{740}$ can be a nanoautoclave.

References

- Iijima S (1991) Helical microtubules of graphitic carbon. *Nature* 354:56–57. doi:10.1038/354056a0
- Pham-Huu C, Keller N, Estournes C, Ehret G and Ledoux MJ (2002) Synthesis of CoFe_2O_4 nanowire in carbon nanotubes. A new use of the confinement effect. *Chem Commun* 1882–1883. doi: 10.1039/b203787b
- Hu J, Bando O, Zhan J, Zhi C, Golberg D (2006) Carbon Nanotubes as Nanoreactors for Fabrication of Single-Crystalline Mg_3N_2 Nanowires. *Nano Lett* 6:1136–1140. doi:10.1021/nl060245v
- Podlivayev AI, Openov LA (2006) Formation of a “cluster molecule” $(C_{20})_2$ and its thermal stability. *Phys Solid State* 48:2226–2232. doi:10.1134/S1063783406110345
- Lu X, Chen Z (2005) Curved Pi-Conjugation, Aromaticity, and the Related Chemistry of Small Fullerenes ($<C_{60}$) and Single-Walled Carbon Nanotubes. *Chem Rev* 105:3643–3696. doi:10.1021/cr030093d
- Veziroglu TN, Zaginaichenko SY, Schur DV, Baranowski B, Shpak AP, Skorokhod VV (2004) NATO science series II: mathematics, physics and chemistry hydrogen materials science and chemistry of carbon nanomaterials. Kluwer Academic Publishers, Springer, Netherlands, pp 329–332
- Zhou I, Pan ZY, Wang YX, Zhu J, Liu TJ, Jiang XM (2006) Stable configurations of C_{20} and C_{28} encapsulated in single wall carbon nanotubes. *Nanotechnology* 17:1891–1894. doi:10.1088/0957-4484/17/8/014
- Glukhova OE, Zhbanov AI (2003) Equilibrium state of C_{60} , C_{70} , and C_{72} nanoclusters and local defects of the molecular skeleton. *Phys Solid State* 45:189–196. doi:10.1016/j
- Qian D, Liu WK, Ruoff RS (2003) *C R Phys* 4:993–1008. doi:10.1134/1.1537434
- Allen MP, Tildesley DJ (1987) Computer simulation of liquids. Oxford University Press, New York