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A SPIN POLARIZATION INVERSION OF ULTRA-SHORT SINGLE-WALLED CARBON NANOTUBES (0, 9) IN A STRONG ELECTRIC FIELD

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Abstract. Results of the numerical simulation of the electronic structure of ultra–short single-walled carbon nanotubes (0, 9) of D_{3h}, D_{3d} and D_3 symmetries at singlet and triplet spin states under an applied electric field were presented. The dependencies of the energy gap, ionization potential, electron affinity and work function on the length of nanotubes at the singlet and triplet spin state were described. It was revealed, that the spin-dependent field-induced electronic structure restructuring determines the change of the spin channel resistance. The critical electric field value ~0.5 V/A inverts spin polarization The carbon nanotubes can act as spin filter and can be used for spintronic logic gates design, that makes nanotubes promising material for spintronic implementation.

Keywords: spin, spintronic, spin polarization cabron nanotubes.

INTRODUCTION

The most important functional property of the spintronic systems is a magnetic coupling, the difference in energy between spin ordered states. In pursuit of semiconductor spintronics, the intensive efforts have been devoted to develop room-temperature magnetic semiconductors and to incorporate carbon-based materials as spin-transporting channels and spin injectors [1]. The spin non-compensation for a wide class of carbon materials such as graphene nanoribbons, graphene nanoflakes, single walled carbon nanotubes (SWCNTs) enlarges the semiconductor carbon-based spintronics application area [1, 2]. The logic gates design methods and topological realization were presented for magnetic coupling 93–339 meV based upon the popular, yet topologically frustrated, family of structures based on triangular zigzag graphene nanoflakes. It was shown, that the logic function can be programmed by external field alignment between graphene layers can become coupled, allowing for more complicated device designs.

The spin order management can be realized by the external magnetic field and even static electric field might have the potential to influence the spin properties too.

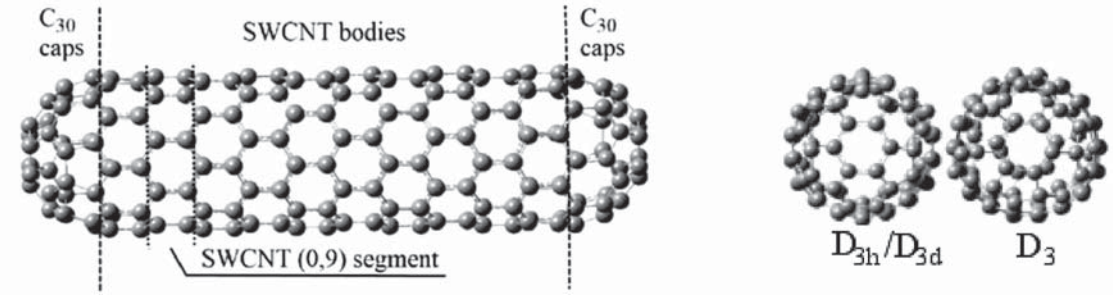
The described graphene structures are unstable and their synthesis is complicated and still not a solved technological problem. As for SWCNTs, the modern synthesis techniques allow to get the narrow distribution in tube length and chirality. Lots of theoretical studies demonstrate the significant changes of the electronic structure of ultra-short SWCNTs (us-SWCNTs) with the length less than 10 nm [3–17]. This actively investigated new class of carbon nanomaterials is thermodynamically stable that was proved in number of papers. The high SWCNTs polarizability determines the sensibility of their electronic structure to external electric fields due to Stark splitting. Therefore there is a reason to operate spin ordering and spin polarization in us-SWCNTs by the external electric field.

The aim of this work is the study of the size-dependent electronic structure alteration and spin polarization of capped us-SWCNTs at ground and exited by strong electric field states.

COMPUTATIONAL DETAILS

The numerical simulations of the electronic structure of the capped zigzag us-SWCNT (0, 9) were carried out using DFT (density functional theory) method in the local spin density approximation (LSDA) with 3–21G basis set by means of the Gaussian 09 program package in the Supercomputing center of Voronezh State University.

A stoichiometric formula of the capped us–SWCNT (0, 9) is C_{60+18i}. Caps are obtained by the dissection of the fullerene molecule perpendicular to the C_{3v} axis



a *b*

Fig. 1. Structural images of capped us–SWCNTs (0, 9) (*a*). The mutual orientation of two C_{60} hemisphere caps D_{3h}/D_{3d} and D_3 symmetries (*b*)

(fig. 1). Regardless of the number of the ring segments *i* there may be two orientations of the caps, corresponding to: 1) D_{3h} (when $i = 2p + 1$) and D_{3d} (when $i = 2p$), (where *p* is integer) and 2) D_3 (for all *i*) symmetries. The nanotube length varied from 1 to 3 nm. According to the Coopmans theorem, the ionization potential *IP* and electron affinity *EA* equals to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy with the opposite sign. In the limit case of zero number of segments the capped us-SWCNT (0, 9) represents the fullerene C_{60}. Therefore, fullerene used as a test object which has been well studied both theoretically and experimentally [18–20]. The values calculated in this paper for the fullerene C_{60} *IP* = 6.69 eV and *EA* = 4.86 eV differ from the average experimental values *IP* = 7.56 ± 0.06 eV [21–24] and *EA* = 2.68 ± 0.02 eV [25, 26]. According to the assumption of Cioslowski et al. [11], the difference between average experimental data and calculated values for the fullerene C_{60} and us-SWCNTs (0, 9) are equal. We used following corrections: ΔIP = 0.87 eV и ΔEA = –2.18 eV in our research. Spin polarization was calculated separately for two spin channels as the difference between the density of electron states (DOS) majority and minority spin electrons related to the total DOS at the corresponding Fermi level.

RESULTS AND DISCUSSION

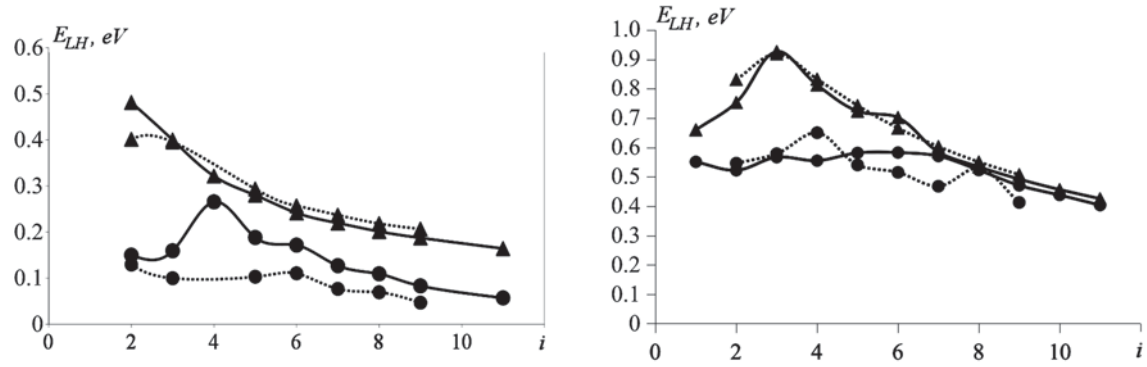
The electronic structure of the capped us-SWCNT (0, 9) at the singlet state

The stability estimation was carried out in terms of binding energy, the difference between total energy and the sum energies of separate atoms related to the number of atoms. The numerical all-electron calculations demonstrate that us-SWCNTs with the D_{3h} and D_{3d} symmetry are more stable than D_3 ones in all the investigated length range. The exception is the nanotube C_{78} that is an agreement with the calculations of the standard enthalpy formation of the us-SWCNT (0, 9), which were carried out in the paper [11]. It was found out that the length increase causes the monotonic decrease of the energy gap. The range of the gap E_{LH} energies is from 1.58 eV to 0.59 eV and from 0.81 eV to 0.29 eV for nanotubes of D_{3h}/D_{3d} and D_3 symmetries respectively. The energy gap is non-zero just in rather small-scale length ranges and seeks to zero at the sizes more than 3 nm, that is caused by the restriction of electrons motion along the tube axis and the impact of the caps interaction.

This fact mutually with the thermodynamical stability us-SWCNTs (0, 9) makes possible to classify them as a whole family of semiconductor nanomaterials. The dependencies of the ionization potential, electron affinity and work function versus the tube length are monotonically decreasing. The values belong to the range *IP* = 6.49–7.30 eV, *EA* = 4.67–4.97 eV, *W* = 2.65–2.84 eV for us-SWCNTs with the D_{3h}/D_{3d} symmetry and *IP* = 6.37–7.29 eV, *EA*=4.69–5.37 eV, *W* = 3.02–3.44 eV for nanotubes with the D_3 symmetry. Remarkably, that in the approximation of the infinite length and flat elementary cell zigzag SWCNT (0, 9) has zero energy gap or *Eg* = 100–140 meV if curvature effects are taking into account [27–30].

The electronic structure of the capped us-SWCNT (0, 9) at the triplet state

The energies of molecular orbitals with the majority and minority spin for the triplet state of the us-SWCNT (0, 9) are shifted up and down in the relation to energies of the singlet state. This shift of orbital energies is determined by the us-SWCNT symmetry. In the triplet state of the nanotube of the D_3 symmetry energies of the LUMO and HOMO for electrons with majority and minority spins are quantity shifted almost symmetrically in the relation to the energies of frontier orbitals at the singlet state. Thus dependencies of energy gaps $E_{LH}(\uparrow)$ and $E_{LH}(\downarrow)$ converge to near values with the rise of the number of segments (figure 2).



a *b*

Fig. 2. Dependencies of energy gaps E_{LH} at the triplet state without electric field (solid lines) and for field 0.5 V/Å (dashed lines) $E_{LH}(\uparrow)$ (circles), $E_{LH}(\downarrow)$ (triangles) on the number of segments of the capped us–SWCNTs (0, 9) of D_{3h}/D_{3d} (*a*) and D_3 (*b*) symmetries

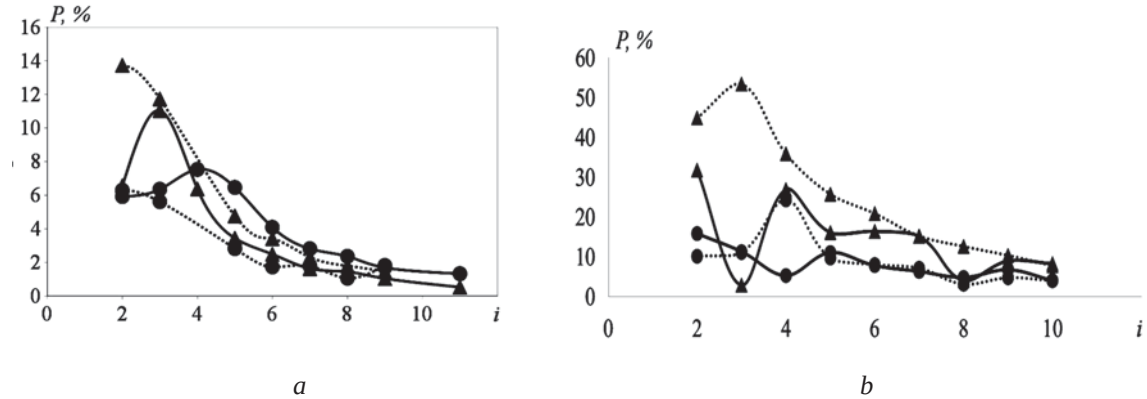
The relation of spin-dependent transport properties versus to the length are qualitatively different for nanotubes of D_{3h}/D_{3d} and D_3 symmetries. It was found that at the singlet-triplet transition the conductivity of us-SWCNTs (0, 9) of the D_3 symmetry decreases that is determined by the increase of the energy gap between frontier orbitals, so $E_{LH}(\uparrow)$ and $E_{LH}(\downarrow)$ changes to 0.1–0.5 eV in relation to the energy E_{LH} at the singlet state. The gaps decrease between frontier orbitals of the us-SWCNTs of D_{3h}/D_{3d} symmetries during the singlet-triplet transition is caused by the unsymmetrical changes of orbital energies. As a result, the energies of the HOMO(↓) and LUMO(↑) are close to HOMO and LUMO levels of the singlet state. The decrease of spin-dependent gaps between frontier orbitals to 0.4–1.5 eV with respect to the energy E_{LH} of the singlet state points out to the significant increase of their conductivity.

As follows from the analysis of the electron density of states, the value of the electron spin polarization of the nanotubes D_3 harshly decreases with the increase of the tube length (fig. 3). What is due to the decrease of the difference of energy gaps $E_{LH}(\uparrow) - E_{LH}(\downarrow)$ from 0.231 to 0.011 eV in the range of segments number i = 2–8. For us-SWCNTs (0, 9) of the D_{3h}/D_{3d} symmetry with the number of segments $i \geq 4$ the value of the spin polarization increases almost linearly with the rise of the nanotubes length. Thus the difference of gaps between frontier orbitals $E_{LH}(\uparrow) - E_{LH}(\downarrow)$ is 0.056 eV and 0.107 eV at i = 4 and i =11.

The external electric field at triplet state causes Stark-splitting of frontier orbitals which leads to decreasing of the energy gap for the majority spin channel and small gap increasing for the minority spin. The opposite modulation causes the difference in spin channels conductivity.

It was found out that spin polarization decreases with the discret increase of tube length by the addition of ring segments as it is shown in figure 1a from 14 % to 1.3 % for D_{3h} symmetry and from 50 to 4 % for D_3 at the field strength E = 0.5 V/Å.

Summary spin polarization is determined by the differecnce between the majority and minority chan-



a *b*

Fig. 3. Dependencies of spin polariztion P at the triplet state without electric field (solid lines) and for field 0.5 V/Å (dashed lines) P(↑) (circles), P(↓) (triangles) on the number of segments of the capped us–SWCNTs (0, 9) of D_{3h}/D_{3d} (*a*) and D_3 (*b*) symmetries

nels polarization. This polarization difference is up to 5 % for D_{3h}/D_{3d} and decreases with the increase of the tube length. The significant polarization difference up to 40 % for D_3 with the number of segments $n = 3$ was found.

So, the Stark-splitting of us-SWCNTs frontier orbitals is sensitive to the spin orientation and determines the decrease of the polarization for majority spin electrons and its increase for minority spin. The polarization increases up to 2 times for the field value 0.5 V/Å. The polarization of main channel inverts at the critical field value ~0.5 V/Å, thus the minority spin channel polarization is 5–40 % (for D_3) and 1–7 % (for D_{3h}/D_{3d}) higher than the majority channel, the minority spin channel acts as the main one.

CONCLUSIONS

The size confinement in the capped zigzag us-SWCNTs (0, 9) causes the size-dependent restructuring of the electronic structure. All main us-SWCNT parameters at singlet and triplet spin states, such as the energy gap, ionization potential, electron affinity and work function are monotonically decreases with the increase of the nanotube length. It was demonstrated that at critical external field value the spin polarization inversion is obtained, the main channel polarization turns from the majority to minority spins. Thus the external electric field can be used to control spin coupling. This fact makes possible the spintronic gate construction which switch their state by electrical field, as in the digital logic semiconductor transmission gate logic.

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ИНВЕРСИЯ СПИНОВОЙ ПОЛЯРИЗАЦИИ УЛЬТРАКОРОТКИХ ОДНОСТЕННЫХ УГЛЕРОДНЫХ НАНОТРУБОК (0,9) В СИЛЬНОМ ЭЛЕКТРИЧЕСКОМ ПОЛЕ

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Аннотация: Методом теории функционала проведено численное моделирование электронной структуры закрытых ук-УНТ(0,9) симметрий D_{3h}/D_{3d} и D_3 в спинсинглетном и спинтриплетном состоянии для различных величин внешнего электрического поля. Установлена монотонная убывающая зависимость спиновой поляризации при дискретном наращивании длины трубки. Показано, что модуляция поляризации в электрическом поле имеет спинзависимый характер: для электронов со спином “вверх” при приложении поля поляризация снижается, для электронов со спином “вниз” поляризация возрастает. При критической величине электрического поля происходит инверсия спиновой поляризации, главным каналом проводимости становится канал со спином “вниз”.

Развитые методы синтеза, высокая стабильность и возможность управления спиновой поляризацией приложением внешнего электрического поля позволяют рассматривать ук-УНТ как перспективный материал для создания спиновых вентилей и других функциональных устройств спинтроники.

Ключевые слова: спин, спинтроника, спиновая поляризация, углеродные нанотрубки.

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