УДК 577. 323

AB INITIO STUDY OF ELECTRONIC STRUCTURE OF DEFECT CARBON (14, 0) NANOTUBE AND (5, 5)/(10, 0) INTERMOLECULAR JUNCTION

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We study the electronic structure of a variety of defect structures of (14, 0) single wall carbon nanotube and intermolecular (5, 5)/(10, 0) junction by Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation using Gaussian type orbitals and periodic boundary conditions (PBC). We demonstrate the adaptability of the PBE PBC for the electronic structure calculations of the 1D carbon defects structures. Comparison of our results with experimental density of states obtained by scanning tunneling spectroscopy indicates that the presence of defects can significantly change the density of electronic states of the SWNTs.

The experimental scanning tunneling microscopy and scanning tunneling spectroscopy (STM+STS) atomic and electronic structures of a defect in (13, 13) metallic nanotube and intermolecular junction (IMLJ) between (21, -2) and (22, -5) nanotubes have been reported in [1-3]. It has been shown that a defect in perfect (13, 13) metallic SWNT creates additional spectroscopic peculiarities between the first two van-Hove singularities [1, 3]. The energetic positions and intensities of the new peaks are functions of a distance from the defect at which they are recorded. These oscillations were explained in terms of resonant backscattering of an incident electronic plane wave from quasibound defect state [1, 3]. STS experimental DOS [2, 3] of IMLJ (21, -2)/(22, -5) recorded near the junction reveals mixture of spectroscopic peculiarities of both metallic (22, -5) and semiconducting (21, -2) structures. The relative weight of the peculiarities depends on the spatial position of recording of the spectra. A decay of the IMLJ local electron states occurs at the distance of several nanometers.

Another type of the defects has been studied experimentally in [4, 5]. It has been shown that exposure of semiconducting SWNTs by O_2 and NO_2 increases density of states at Fermi level and makes these species metallic. Based on the *ab initio* pseudopotential calculations [6] of chemisorbed O_2 molecule these results have been interpreted as an adding of hole carriers at the Fermi level of a *p*-semiconducting SWNTs and closing the forbidden gap due to this reason. A prediction of the gap closing in semiconducting SWNTs due to a creation of Stone-Wales defect [7] has been made using Tight-Binding (TB) model and LDA calculations. The TB results of a set of IMLJ structures have been observed in [8]. The theoretical results [8] qualitatively confirm experimental [3] results.

Nevertheless some experimental results even of achiral SWNTs [9] have not been explained successfully. The simplest example of SWNT [9] corresponds to the (14, 0) SWNT (specimen No 7, diameter d=1.1 *nm*, and chiral angle φ=30°). In accordance to the $2m+n$ rule [10] that SWNT should be a semiconductor, but the experimental DOS of the SWNT reveals metallic properties. We assume that such discrepancy of experimental and theoretical results can be explained by presence of defects in atomic structure of the individual (14, 0) SWNT [9].

To examine the hypothesis we performed *ab initio* PBE [11] 3-21G, 6-31G and 6-31G* calculations [12] taking into account periodic boundary conditions of 1D structure of pristine (14, 0) and a set of a defect structures (Stone-Wales defect, double vacancy (2V), ***ad dimmer*** defect (2 additional carbon in the carbon wall) and two defect structures caused by saturation of one double C-C bond by OH and H groups (2OH and 2H). For correct description of isolated defects the lengths of unit cells of the objects have been chosen up to 20 E. To model a change in defect concentration, the unit cells with different lengths (and different numbers of carbon atoms) have been chosen. To study a changing of atomic symmetry of a nanotube by insertion of 5/7 defect we performed *ab initio* PBE PBC 3-21G calculations of the IMLJ (5, 5)/(10, 0) structure.

The geometry optimization of the defect structures has been performed by analytic energy gradient and the PBE functional [11] using a 3-21G basis set. The number of atoms in the unit cells varies from 226 for the 2H defect (saturated C-C bond by two hydrogen atoms) (2020 basis set functions in 6-31G basis set) to 334 atoms for the structure with double vacancy (3006 basis set functions in 6-31G basis set). The electronic structure has been obtained using 128 points in ***k***-space for the Brillouin zone. The electronic structure of pristine (14, 0) SWNT has been calculated by both PBE [11] and PBE0 [13] functionals. The last one gives much better agreement with the experimental DOS for the semiconducting SWNTs in comparison with the PBE functional [14]. The unit cell of the IMLJ (5, 5)/(10, 0) structure contains 360 carbon atoms ((3240 basis set functions in 3-21G basis set). The length of the unit cell is equal to 40 E. The geometry optimization of the IMLJ structure has been performed by semiempirical PM3 method for a structure containing 3 unit cells (more than 900 carbon atoms) and using analytic energy gradient. For the IMLJ the electronic structure has

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been obtained using 64 points in ***k***-space for the Brillouin zone. To interpret the DOS of IMLJ (5, 5)/(10, 0) the electronic structure PBC PBE calculations of (5, 5) and (10, 0) pristine structures have been performed using 6-31G* basis set. The electronic structure of (5, 5) and (10, 0) SWNTs has been obtained using 128 points in ***k***-space for the Brillouin zone.

In Fig. 1, the STS experimental ((a), [9]) and theoretical DOSes obtained with the PBE and PBE0 functionals ((b) and (c)) for the (14, 0) zigzag semiconducting SWNT are presented. Surprisingly, the experimental DOS of the (14, 0) sample displays the metallic nature. The PBE and PBE0 electronic structure calculations display semiconducting properties of the electronic structure of the (14, 0) SWNT in accordance with well known theoretical result [10].

In Fig. 2, the STS experimental ((a), [9]) and theoretical DOSes of a set of defect structures (Stone-Wales defects (b), 2H defect (c), 2OH defect (d), **ad dimmer** defect (e) and 2V defect (f)) are presented. Introduction of the defect structures (Figs. 2b, 2c, 2d, 2e and 2f) into the atomic lattice of the pristine structure leads to the creation of embedded states inside the gap. In all cases we can describe qualitatively (or semiquantitatively) the main peculiarities of the experimental DOS displayed at ~ -0.9 and 1.4 eV. The (14, 0) structure with Stone-Wales defects remains semiconducting, whereas all others defects convert the semiconducting electronic structure of pristine (14,0) SWNT into metallic one.

Modulations of the local DOS of SWNT near defects has been observed in [2] and qualitatively attributed to the interference between incident and scattered electron waves in the nanotubes. The energy dispersion of the SWNTs with defects has been interpreted in terms of quantum interference of electrons scattered by defects in [1]. A specific energy-dependent oscillations [15] is modeled using 1D plane wave exp(ikx), where x is position. The incident plane wave can resonantly backscatter from the quasibound state with reflectivity $|R|^2$ ($R=|R|\exp(-i(kx+\delta))$, where δ is the phase shift). The corresponding standing wavefunction is written as $\psi(k, x)=\exp(ikx+|R|\exp(-i(kx+\delta)$, which corresponds to a spatial oscillations in the DOS $\rho(k, x)=|\psi(k, x)|^2=1+|R|^2+2|R|\cos(2kx+\delta)$ [15].

To study an influence of concentration of defects on the electronic structure of SWNT we performed the PBE PBC calculations of two 2V defect structures. The first one, with one 2V vacancy in the unit cell (334 atoms) corresponds

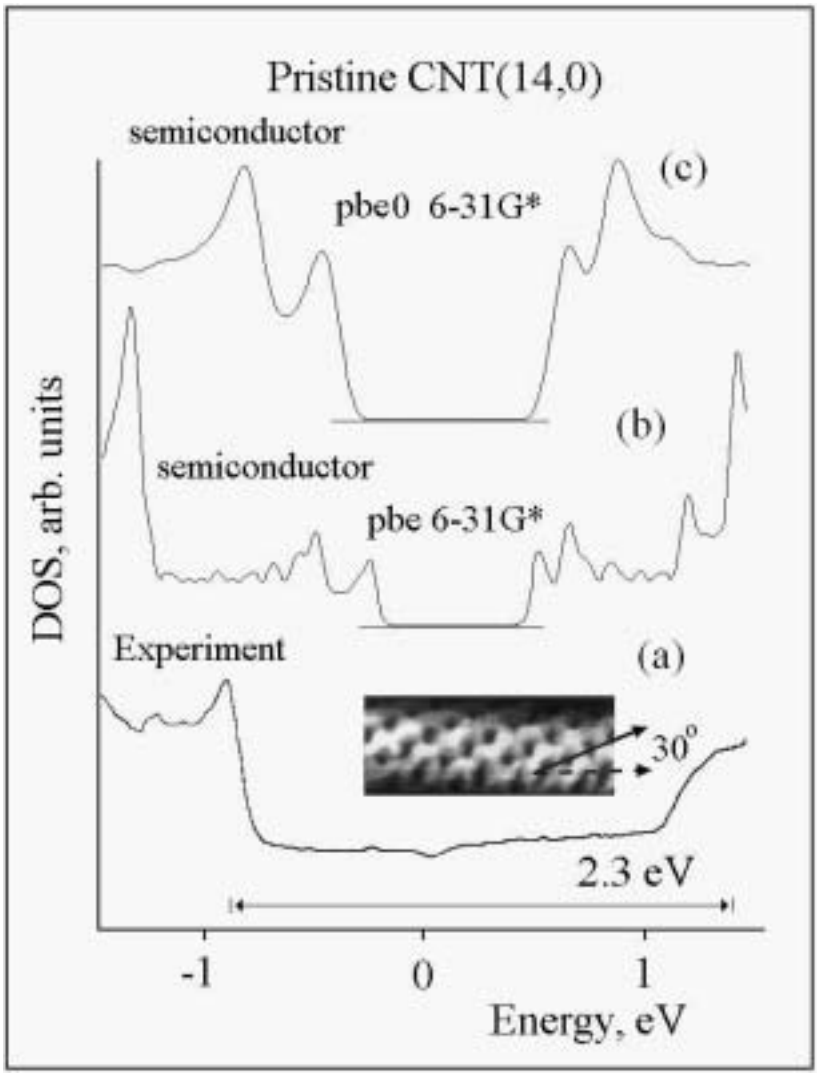

Fig. 1. The STS experimental [9] (a) and theoretical PBE (b) and PBE0 (c) DOSes of semiconducting zigzag (14,0) SWNT. The insert shows an STM image of the sample. It has been clearly seen that the SWNT has atomic structure of zigzag type.

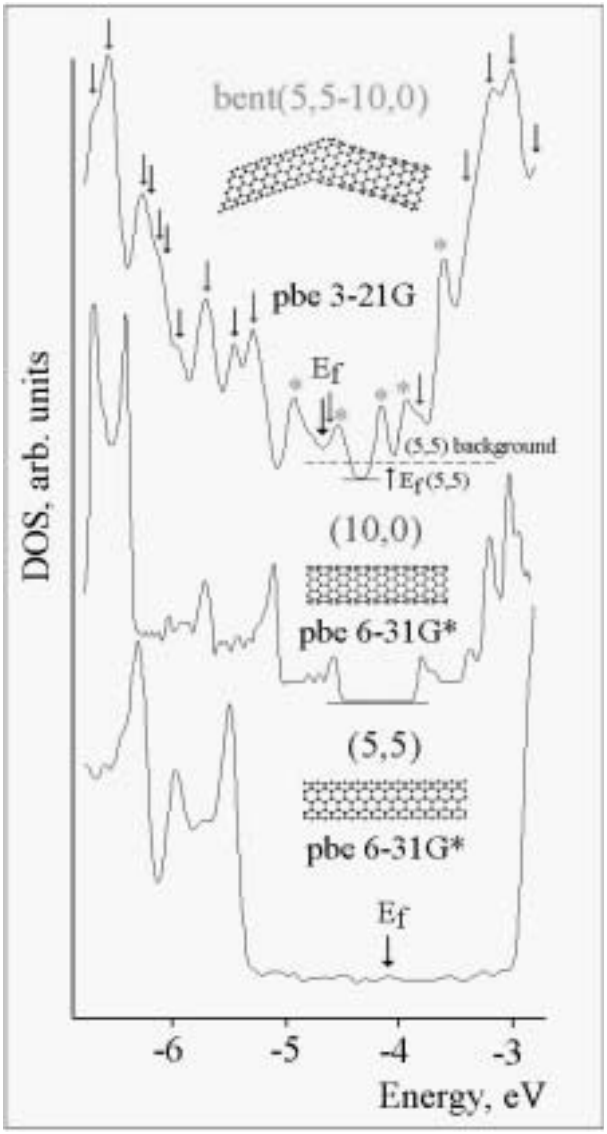

Fig. 3. Density of states of (5, 5), (10, 0) and IMLJ bent (5, 5)/(10, 0) structure. Blue arrows mark peculiarities attributed to the (5, 5) SWNT, red arrows mark peculiarities attributed to the (10, 0) SWNT, green stars mark peculiarities attributed to the peculiarities caused by the IMLJ structure. Black arrow marks a position of the Fermi level of the bent IMLJ (5, 5)/(10, 0) structure. The insert shows the IMLJ bent (5, 5)/(10, 0) structure.

The performed PBC PBE calculations demonstrate the excellent adaptability for the 1D electronic structure calculations of defect carbon nanostructures. To study the effect of intermolecular junction we modeled the periodic IMLJ (5, 5)/(10, 0) structure (see insert on Fig. 3). The length of the translation vector of the system is ~ 40 E. Application of the translational symmetry for the unit cell creates an infinite zigzag carbon nanostructure with alternation of (5, 5) and (10, 0) sites which are separated by structures containing 5- and 7-member rings.

In Fig. 3, the density of states of (5, 5) and (10, 0) SWNTs as well as the DOS of IMLJ (5, 5)/(10, 0) structure are presented. The IMLJ structure has metallic DOS (the Fermi energy is located at -4.7 eV). The electronic states near the Fermi energy are determined by the IMLJ structure. The electronic states below and above the Fermi energy are determined mainly by the pristine (5, 5) and (10, 0) sites (Fig. 3).

The comparison of the theoretical results with experimental ones shows the adaptability of PBC PBE calculations for the electronic structure calculations of the semiconducting carbon nanostructures with defects of several types. Essential differences in density of states of pristine structures and structures with defects can serve as a simple test for the presence of defects in atomic structure of the SWNTs using STS experiments.

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НЕЭМПИРИЧЕСКОЕ ИССЛЕДОВАНИЕ ЭЛЕКТРОННОЙ СТРУКТУРЫ РЯДА ДЕФЕКТНЫХ СТРУКТУР ОДНОСТЕННОЙ УГЛЕРОДНОЙ НАНОТРУБЫ (14, 0) И МЕЖМОЛЕКУЛЯРНОГО (5, 5)/(10, 0) КОНТАКТА

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В статье приводятся результаты зонных DFT (PBE потенциал) расчетов электронной структуры набора дефектных структур одностенной углеродной нанотрубы (14, 0) и межмолекулярного (5, 5)/(10, 0) контакта с использованием гауссового типа орбиталей. В работе демонстрируется применимость данного подхода для подобного рода объектов. Сравнение наших результатов с экспериментальными спектрами сканирующей туннельной спектроскопии показало, что наличие дефектов может существенным образом влиять на плотность электронных состояний углеродных нанотруб.