NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2017, 8 (5), P. 641–646

Modeling chemisorption of carbon dimer at $(8,0)$ nanotube

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PACS 71.15.Ap, 71.15.Nc, 73.20.Hb, 74.20.Pq, 81.07.De **DOI 10.17586/2220-8054-2017-8-5-641-646**

The electron structures of two forms of the grafted carbon dimer for the (8, 0) zigzag nanotube were calculated by the semi-empirical quantum-chemistry method applied to the supercell model. If the dimer adsorbs above the center of the tube's hexagon (h-grafting), it performs the topochemical transformation of the tube, according to the Stone–Wales scheme of inverse kind. B-grafting is a chemisorption above tube's bond, it is energetically lower, than h-grafting. Atomic structure of b-grafting is a splitted di-interstitial. Measuring the electronic density of states in the upper valence bandhas been shown to make it possible to distinguish between pure and grafted nanotubes, as well as between b- and h-graftings.

Keywords: Carbon nanotubes, quantum chemistry, chemisorption.

Received: 11 September 2017

Revised: 25 September 2017

1. Introduction

The carbon dimer (C_2 molecule, when isolated) is an important structural element of graphene and carbon nanotubes. Several point defects, occuring in these materials during growth or mechanical influence, can be represented by the carbon dimer (C–C bond) as a basic point defect. The well-known intrinsic topochemical defect (A. J. Stone, D. J. Wales, 1986) appears in an ideal hexagonal carbon net when dimer rotates on 90°. After the rotation the dimer is included in two 5- and two 7-membered carbon cycles: defect SW(55-77) [1], or (5-7-7-5) [2,3]. Ad-dimers (C_2 molecules after adsorption) produce interstitial defects in graphene and nanotubes; they may remain after growing the material, or may be entered purposly. Ion beam of C_2^- was used for structural modification of the fullerene film, and it has been found that new bonds were formed by dimers [4]. Hydrocarbon chemisorption could be the first stage of entering ad-dimers into graphene or nanotube: dehydrogenation is possible by electric current through the STM tip [5], or (supposedly) by tip-focused electron, X-ray, or molecular beam.

Theoretical models of the ad-dimer grafting by 2-dimensional-graphene net propose to place the dimer in the center of the bond's hexagon, in order to switch chemical bonds similarly to SW transformation. Such an interstitial-like defect is called (7-5-5-7) [2,3,6], or "inverse Stone–Wales" ISW [1,7]. (The dimer inside the SW is the common side of the 7-membered cycles, and inside the ISW is the common side of the 5-membered cycles.) This kind of dimer incorporation will be called below h-grafting.

The 3-dimensional-graphite problem of radiation defects, related to the interstitial dimer [8], also required models for dimer grafting. "Grafted interlayer bridge" di-interstitial [9], later marked $I_2(7557)$ [10], is similar to ISW in graphene. However, the alternative structure – splitted di-interstitial – was found [9], later marked $I_2(\alpha\beta)$ [10]. Suppose that the dimer is situated immediately above C–C bond of hexagonal net (basal atomic plane of graphite), so that it forms a 4-member cycle, perpendicular to basal plane. Splitting of di-interstitial means that the cycle slides as a whole, making dimer and the bond be equally spaced in the coordination-complex manner among 4 "ligand" neighbors of the net. This kind of dimer incorporation will be called below b-grafting.

2. Goal, method, and model

Theoretical calculations, presented here, are devoted to the covalent grafting of carbon dimer by the small-diameter SWNTs (single-wall carbon nanotubes) $(8,0)$ zigzag (chemisorption is equivalent to grafting in such low-dimensional system). Two possible above-mentioned ways of dimer incorporation are studied: h-grafting (dimer is placed above hexagon center), and b-grafting (dimer is placed along chemical bond). The tube's chirality allows high-symmetry models with degenerate electronic states, so insulating and metallic configurations may be compared. Although topologically similar, carbon nets of graphene and small-diameter SWNTs have different many-electron properties. The results of calculations of ad-dimer grafting in graphene and graphite [1,9,10] may be extrapolated to large-diameter SWNTs [2,3], but the case of large curvature should especially be considered.

The tool for the total-energy electron-structure calculations is a program set that:

- belongs to quantum chemistry,
- deals with MO-LCAO determinant wave function,
- uses the restricted Hartree–Fock–Roothaan algorithm for the self-consistent ground state,
- is advanced for open-shell configurations (several-determinant terms of a given symmetry),
- is constrained by semi-empirical basis of Slater-type atomic orbitals. Semi-empirical INDO parametrization was achieved previously, it is suitable for materials and macromolecules composed of Si and C, where impurities and chemical groups may contain H and N atoms. As to carbon materials, this tool had been used for: vacancy centers of diamond, molecular and crystalline fullerene [60], graphite and graphene, nanotubes. Modeling systems of 10^2–10^3 atoms on ab-initio level requires significant computing power and time, thus semi-empirical quantum chemistry is still useful, at least as a preliminary step. For example, properties of the SW defect in $(8,0)$ and $(5,5)$ nanotubes, exposed to fracture-like deformation, were succesfully investigated using this tool [11].

The model of the SWNT was treated as a 1-dimensional supercell consisting of 8 primitive unit cells. Periodic boundary conditions require that every molecular orbital (MO) possesses a wave vector from the uniform k-set of 8 brillouin-zone points. Since the primitive cell of SWNT $(8,0)$ consists of 4 circles of 8 atoms, the supercell model contains 256 atoms. To reach the goal, 4 ad-dimers were added to the tube's supercell; furthermore they were uniformly distributed over tube's length and axial angle with helical symmetry. Ad-dimers of such a model are identical and nearly independent. Due to 4-fold screw axis the model has degenerate electron states, which makes it possible to compare closed- and open-shell configurations. Figs. 1, 2 show the part of the model (2.5 primitive cells of 8) with one ad-dimer of 4. Atomic balls are drawn by the same program kit that fulfilled calculations (to help eliminate errors in input files), bonding sticks are hand-drawn.

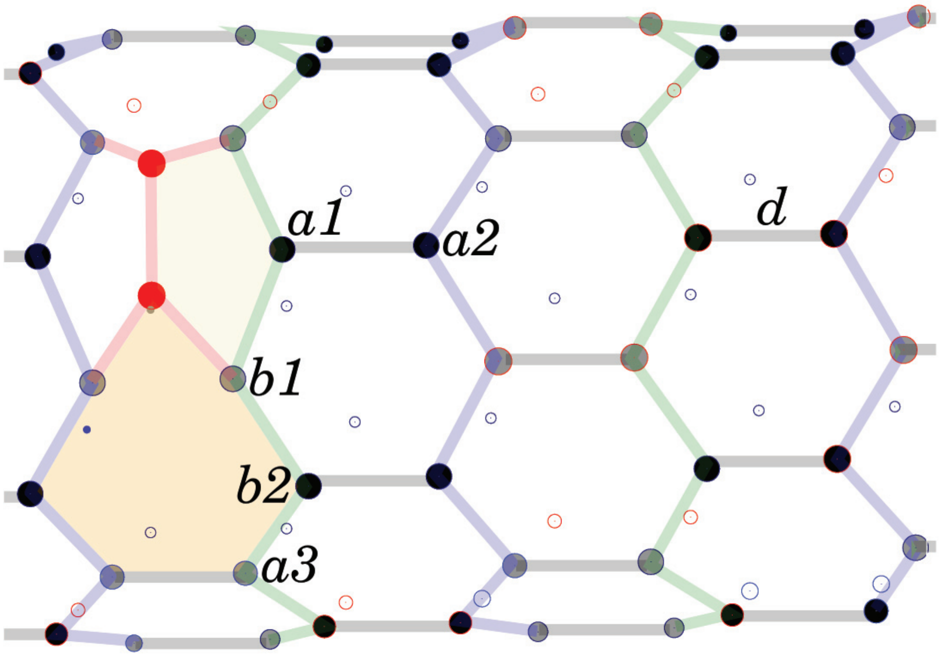

FIG. 1. Ad-dimer's h-grafting, or inverse Stone–Wales transformation. Longitudinal CC bond is used as a length unit d

Each mark in Figs. 1, 2 refers to several neighbors of equal symmetry (coordination star), their positions should be varied simultaneously, one coordination star after another, as well as dimer's length and height, until the total-energy minimum is found. See below about equilibrium structures of both graftings.

Colored 5- and 7-membered cycles around h-grafted dimer of Fig. 1 remind one about the topochemical Stone–Wales ability of ad-dimer placed above the center of hexagon. Colored cycles around the b-grafted dimer of Fig. 2 do not have usual chemical-structure sense. They help to visualize the coordination-complex-like geometry: a 4-member cycle, consisting of dimer and split bond $b2$, plays the role of the "center"; adjoint nested 6-member cycles are non-planar, contain "ligands" $c1$, and are flexed either to the dimer or to the split bond.

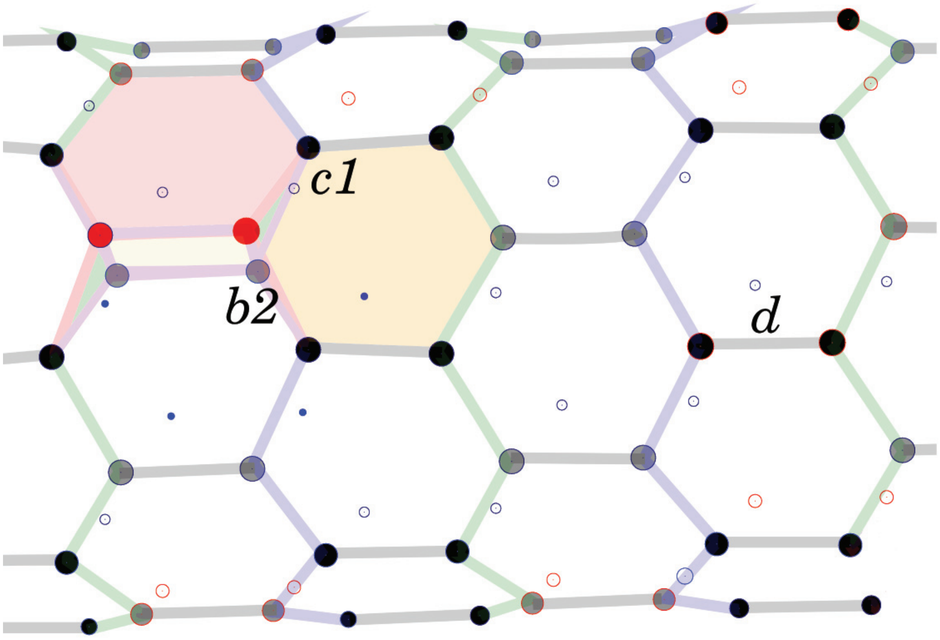

FIG. 2. Ad-dimer's b-grafting, or splitted di-interstitial

3. Atomic structures of grafted dimer

With the use of the same quantum-chemistry tool and the supercell models, optimal (i. e. giving minimal total energy to the model) lattice parameters of graphene and SWNT $(8, 0)$ were previously found. Calculated optimal lengths of the longitudinal tube's bond d and of graphene bond are very close, and rather close to the well-known experimental value 1.42 Å. Calculated SWNT $(8, 0)$ optimal radius $R = 2.24d$, and zigzag $Z = 0.49d$ (in graphene $Z = d/2$). Initially, the goal supercell was taken with large distance between dimers and the tube, thus the total-energy origin (free dimers and tube), as well as dimer's optimal length, were found. Total energies are given below as dimer-bonding energies in eV/dimer, obtained by formula of cohesive (binding) energy of defect, *(total energy – origin) : 4*, since 4 dimers are present in the supercell.

Calculations of the equilibrium (optimal) atomic structures were organized as a repeated search of 1-dimensional minimum of the total energy, taken as a function of a given parameter (length and height of dimer, and shifts of its neighbors). After the optimal value for the chosen parameter had been found, it was fixed, then 1-D minimization was repeated with the next parameter. Each 1-D minimization produces a difference of initial and final total energies, that determines "the cost" of given parameter. Parameters with negligible cost were excluded from optimization, thus the corresponding atoms mainained their positions. At last certain displacements, marked in Figs. 1, 2, with sufficient costs were found. The sequence of their optimization was ordered according to the cost, thus the accelerated the search for equilibrium. The results are gathered in Table 1.

Bonding energies of alternative dimer graftings are the main calculation results. According to the total-energy theory, in 3-D graphite [9, 10], both h- and b-graftings are possible, as having lower energy than independent substrate and dimer, that is also true for SWNT $(8, 0)$. But which of them has lower total energy? Our findings show that b-grafting is ~ 0.9 eV/dimer lower than h-grafting. In graphite, this is reversed: h-grafting is lower by ~ 1.4 eV/dimer [9] or ~ 2.0 eV/dimer [10].

4. Elecronic structures of grafted dimer

The calculated energy spectra of self-consistent MOs are presented below in the form of observable densities of the occupied (valence-band) electronic states (DOS). Since spectra of our grafted-dimer model cover only 8 k-points of its supercell's k-set, they (spectra) are discrete and need smoothing to be transformed into DOS. Gaussian-type smoothing was used with parameter $\Delta = 0.3$ eV (the magnitude itself is not very important):

TABLE 1. Length, height, and shift along tube's axis are given in d (see Fig. 1). Angle of rotation around tube's axis is given in degrees. Signs refer to the marked representatives of coordination stars in Figs. 1, 2. The origin of height is tube's radius R. Positive shift is to the right. Positive angle is clockwise if looked at from the right

	h-grafting						b-grafting		
	dimer	$a1$	$a2$	$a3$	$b1$	$b2$	dimer	$b2$	$c1$
length	1.016						1.110	1.070	
height	0.606						0.365	–0.715	
shift		–0.086	–0.028	–0.010	+0.016	+0.038			–0.020
angle					–1.9	–1.3			–1.5
energy	–8.7 eV/dimer						–9.6 eV/dimer		

$$\nu(E) = \frac{1}{N} \sum_{i}^{\text{occ}} \exp \frac{-(E - E_i)^2}{2\Delta^2}, \tag{1}$$

where N is a number of electrons of the supercell; i numerates all MOs despite degeneration; "occ" means summation over occupied MOs. The results are gathered in Fig. 3. It should be mentioned that the energy origin is a "vacuum level" of a free electron at rest. The left portion of Fig. 3 shows the occupied part of MO-spectrum of the pure SWNT $(8, 0)$ with 1-, 2-, and 4-fold degenerate states ordered in columns. The left-most DOS curve is an application of (1) to this spectrum.

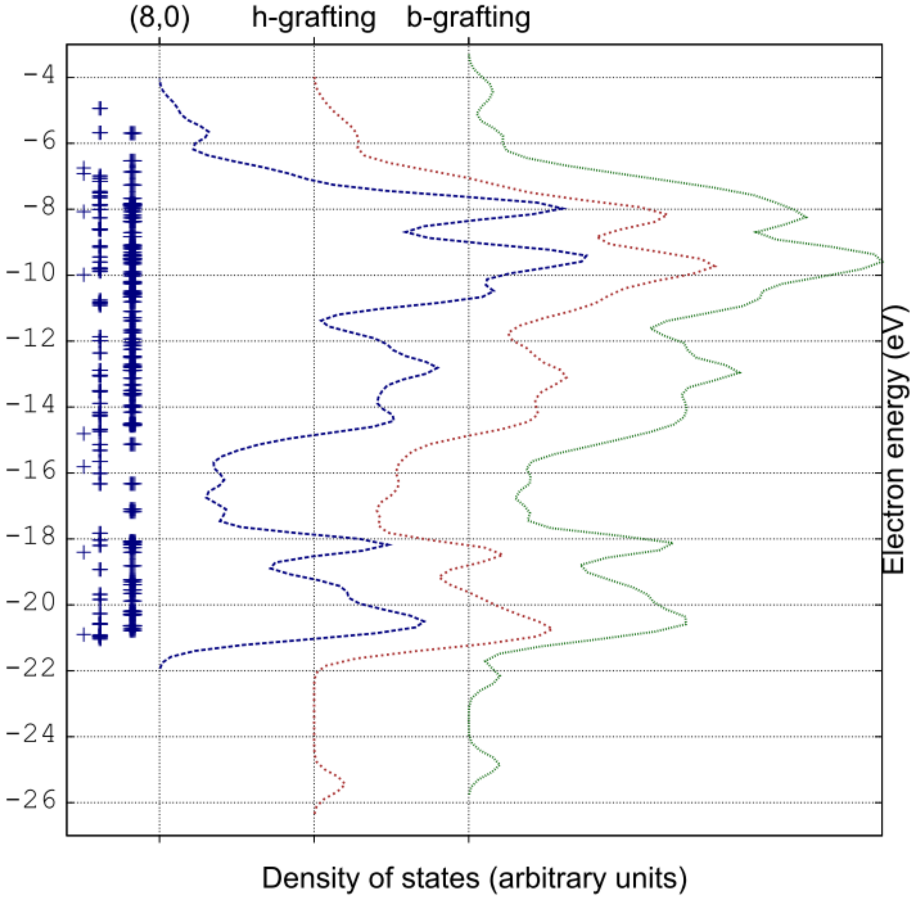

FIG. 3. Densities of occupied states calculated from MO spectra. Origins of three curves are shifted for the sake of comparing: pure SWNT $(8, 0)$, tube with h-grafted, and with b-grafted dimer

To extract DOS from measurements is a standard procedure in scanning-tunneling or atomic-force microscopy, in photoelectron emission spectroscopy, and the like. DOS at the top of occupied energy band is analyzed in the first place in order to fix structural changes, for example: incorporation of carbon dimer into a fullerene film [4], or hydrogenation of adsorbed molecules in STM [5]. Fig. 3 demonstrates DOS changes of this kind in $(-4, -6)$ eV band, where pure tube, as well as the tube with grafted dimer in both forms, do have distinct DOS features. Thus, dimer grafting can be identified indirectly, for instance, if b-grafted species looks in STM like the bond, which it splits down.

Electronic density $n(x, y, z)$ is another observable that can be calculated from occupied MOs. There are two ways to present this function of 3 arguments by a single drawing. Either one draws a 3-dimensional iso-surface, or a 2-dimensional (plain) map of iso-contours. The latter method demands simple graphical applications, so Fig. 4 is one of iso-contour maps that exhibits electronic density of the tube with b-grafted dimer. The plane of the map cuts the tube vertically and passes close to three points (see Fig. 2): one atom of dimer (the topmost), the nearest to it atom of the split bond $b2$ (inside the tube), and the nearest to them "ligand" atom of the tube $c1$. This plane was selected to display the covalent nature of b-grafting, whose structure resembles a chemical complex with a 4-member cycle as a center. Besides, it gives the same aspect of the tube's bond before (bottom segment) and after splitting (top segment).

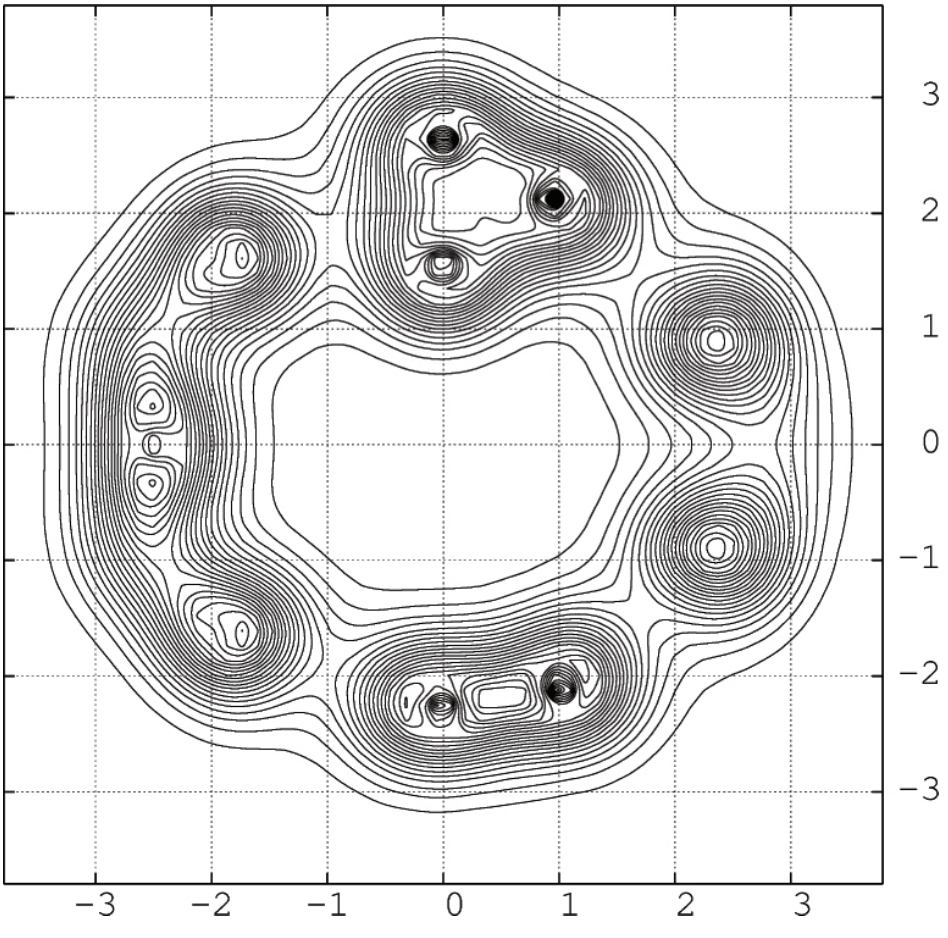

FIG. 4. Electron-density map of b-grafted dimer. The map's plane passes through 3-member cycle (see Fig. 2): atom of dimer – atom $b2$ of the split bond – "ligand" atom $c1$

Other maps of electronic densities also assure the covalent character of the grafted dimer. 5- and 7-membered flexed cycles of h-grafting colored in Fig. 1, as well as 4-membered "central", and 6-member flexed "ligand–center" cycles of b-grafting colored in Fig. 2, all them appear on electron-density maps as combinations of σ- and π-bonds. For example, the topochemical prediction of ISW in graphene is also true for h-grafting, though equilibrium height of ad-dimer, $\sim 0.6d$ above tube's surface, makes 5- and 7-member cycles strongly flexed. If compared to other maps, the 3-member cycle of Fig. 4 could be called "cycle" in geometrical sence only, the electronic thickening around it corresponds to the covalent ligand–center bonding.

5. Discussion

To obtain good agreement with experimental data (not available for ad-dimer recenly) may require calculations of a higher level than those presented above. However, quantum-chemistry results cover not only total energies and geometrical parameters (Table 1), which usually are rather difficult experimental goals. The present calculated energetical (Fig. 3) and spatial (Fig. 4) electron densities are complementary observables, which relate directly to experiment [4,5].

One more argument pro the covalent character of ad-dimer incorporation into the tube may be found in the well-known feature of quantum chemistry called “atomic charges”. It is a standard output indicator of MO LCAO that shows the fraction (in sense of probability) of atomic orbitals of the given atom in occupied molecular orbitals. Small atomic charges support covalent bonding. Maximal absolute value of all atomic charges was < 0.2 for h-grafting, and < 0.1 for b-grafting (in atomic units).

At last it should be noted that the ad-dimer must overcome van-der-Waals barrier, before being covalently bonded (grafted) by the tube. This side of the problem is not addressed at all by our calculations at a semi-empirical level. Implementing certain corrections makes sense at the ab-initio level [10]. Therefore, the semi-empirical results (e. g. Table 1) are just a prelude to analysis and planning of experiment. Which form of grafting will take place depends on many circumstances of tube’s environment in future experiments.

6. Conclusion

Quantum-chemistry modeling of the carbon dimer chemisorption at carbon nanotube shows, that stereo-chemical assumption about covalent incorporation of dimer into graphene net is only sufficient for qualitative predictions. Previous calculations, guided by such assumption, had been performed for the topochemical inverse Stone–Wales grafting of ad-dimer at graphene and nanotubes. But alternative grafting, split di-interstitial, has not any simple stereo-chemical support, and was not studied before in the case of nanotubes. The calculations, presented above, were made for both kinds of ad-dimer grafting at the small-diameter SWNT $(8,0)$. The result is: total energy of b-grafting (split di-interstitial) is on ~ 0.9 eV/dimer lower than of h-grafting (inverse SW).

The electronic structures of both graftings are of the covalent type, though b-grafting with flexed, split, and nested 6-membered cycles is more like a chemical complex with a 4-member cycle as a center. In both cases, the ad-dimer is placed above tube’s surface, so terms ”grafting” and “chemisorption” are fair. In h-grafting, the ad-dimer stays at $\sim 0.6d$ above tube’s surface (where d is the lenght of longitudinal CC bond), that could be called a chemisorption at the hexagon center, if its bonding energy was unknown. In b-grafting, the ad-dimers height is $\sim 0.4d$ above the tube’s surface, with the splitted bond at $\sim 0.7d$ under the tube’s surface.

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