

FIRST PRINCIPLES SIMULATIONS ON DISSOCIATIVE ADSORPTION OF METHANE MOLECULES UPON NICKEL SUBSTRATE RESULTING IN A GROWTH OF NANOTUBES

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To predict the growth mechanism of carbon nanotubes (CNT) upon nickel catalyst, we have performed a series of large-scale DFT-LCAO interface calculations. When using the CVD method for CNT synthesis, carbon adatoms appear upon the nickel catalyst surface due to dissociation of carbon-hydrogen molecules (e.g., CH₄). We have started with the 2D models of molecular adsorption upon smooth and nanostructured Ni(111) substrate. As a next step, we have simulated the C/Ni(111) interface, where carbon adatoms initially form flat carbon nanoflakes. Association of the adsorbed carbon atoms upon the catalyst surface precedes further swelling of the (C_n)_{ads} islands after appearance of pentagonal defects within a honeycomb sheet which are more probable upon the catalyst surface containing either defects or nanoclusters. Thus, nanoflakes can be gradually transformed into nanotube embryos (in the form of semi-fullerenes), and finally into capped CNTs ($d_{c-c} \approx 1.42 \text{ \AA}$) with either armchair or zigzag chirality. Periodicity of the system results in a model of infinite bundles of single-walled (SW) CNT with a diameter 0.80-0.82 Å and inter-tube distance 4.2-4.6 Å (depending on chirality).

1. Introduction

Carbon nanotubes (CNT) became an important constituent of next generation nanoelectronic devices [1] which is still hindered by inability to reproduce reliably growth of CNT with predetermined chirality indices, since existing methods of nanotube synthesis yield a mixture of metallic and semiconducting nanotubes. The chemical vapor deposition (CVD) growth of capped CNTs atop the particles of metallic catalyst is believed to be the promising approach for gaining a control over the properties of nanotubes [2]. Moreover, the CVD growth of nanotubes can be achieved at low temperature, another important requirement for application of CNTs in nanoelectronics. The atomistic structure of junction between the nanoparticle of metallic catalyst and the CNT is

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important for understanding both the electronic transport through the nanotube and the mechanism of its growth.

Decomposition of gas-phase carbon-hydrogen precursors (C_nH_m) on the catalyst surface is the first step for the CVD growth of CNTs. This is followed by two important processes: (i) diffusion of C atoms along the catalyst surface or across its interior (rate-determining step) and (ii) the nucleation of the graphitic fragment followed by further incorporation of carbon into the growing nanotube, which determines CNT chirality [3]. Depending on the size and the structure of catalyst particle, either the well-separated single-wall (SW) nanotubes, their bundles (containing up to several hundreds of the closely-packed nanotubes of different chiralities) or MW (multi-wall) NTs, which shells also possess various chiralities, were synthesized. The formation of SW CNTs mainly requires the presence of transition-metal element or alloy catalysts [4] which are crucial for the controlled synthesis of SW CNTs by means of CVD [5]. However, an exact role of metal atoms in the growth of SW CNTs is still unclear.

In this study, we have performed a series of first principles calculations on 2D periodic models of carbon-containing adsorbate upon both smooth and nano-structured Ni(111) substrate, varied from the CH_4 molecules up to the gradually growing bundles of capped SW CNTs possessing either *ac*- or *zz*-type chirality.

2. Computational details

The first principles of DFT (Density Functional Theory) - LCAO (Linear Combination of Atomic Orbitals) method, as implemented in the *CRYSTAL* code [6], allows us to describe both 1D nanotubes and 2D sheets in their original space form. For *ab initio* calculations on CH_4 molecules and ensembles of C adatoms upon the Ni(111) substrate, we have used the all-valence basis sets of atomic Gaussian-type functions (constructed using pure *s*- and *d*- as well as hybrid *sp*-AOs): Ni (8*s*-64111*sp*-41*d*), C (6*s*-311*sp*-11*d*) and H (31*s*-1*p*) [7].

The gradient-corrected exchange-correlation DFT functional by Perdew, Burke and Ernzerhof (PBE) [8] has been used in our spin-polarized calculations. To provide a balanced summation in both direct and reciprocal lattices, the reciprocal space integration has been performed by sampling the Brillouin zone with the $2 \times 2 \times 1$ Pack-Monkhorst mesh [9], which results in 2 *k*-points in total for 5×5 surface supercell of Ni(111) slab models. Calculations have been considered as converged when in two successive cycles of the self-consistency procedure the total energy differs by less than 10^{-7} a.u. A smearing temperature of 0.001 a.u. has been applied to the Fermi function. This value for the temperature has been chosen relatively low, to ensure that the magnetic moment is not artificially modified by a too high value. All the calculations have been performed with complete geometry optimization.

3. Results of simulations

We have compared and verified the results of *ab initio* simulations, which describe peculiarities of the initial stage of growth for the bundle of SW CNTs upon the catalyst particle. The only limitation of the 2D model is that both the chirality and diameter of carbon nanotubes in the bundle are equivalent.

As a first stage for these simulations, we have considered adsorbate-free models of both smooth and nano-structured Ni(111) surfaces. The supercell of smooth nickel slab has been constructed from cubic *fcc* Ni crystal (space group *Fm3m*, the lattice constant 3.532 Å, $\alpha = \beta = \gamma = 90^\circ$). 5-layer slab contains 125 atoms *per* SC. The nano-structured surface contains a cluster *per* 5×5 supercell atop the smooth (111) surface which includes 7 and 3 nickel atoms in the corresponding sites of the 1st and 2nd (111) sublayers, respectively.

The network of the adsorbed carbon atoms, which gradually transforms to CNT structures, can appear due to dissociation of hydrocarbon molecules, *e.g.*, simplest CH₄ (point group *T_d*, equilibrium length of C-H bond 1.086 Å [10]), flowing towards the substrate in the CVD method [2]. The energetically most preferable site for adsorption of methane molecule on Ni(111) surface has been found to be the hollow *fcc* site. We estimate the dissociation energies for methane molecules atop both smooth and nano-structured substrates. Their comparison clearly shows that the presence of small periodically distributed nanoclusters results in preferable carbon atomization.

Translation vector for a regular C adsorbate structure upon a smooth nickel surface has a length 2.47 Å which is structurally compatible with the (111) face of adsorbent (length of analogous vector on nickel substrate is 2.49 Å), *i.e.*, their mismatch is only ~0.8 per cent. To form the quasi-graphene structure, the neighboring C adatoms can be positioned above the neighboring *fcc*- and *hcp*-adsorption sites, *i.e.*, packing of adatoms must be as twice as larger than in the case of regular adsorption upon the same type of surface sites. To form semi-fullerene-like embryos from quasi-graphene islands upon the surface of Ni catalyst, they must contain pentagons which result in swelling of the islands with further growth of fullerene-like structures [11]. We have considered this process atop a Ni(111) substrate by gradually increasing the number of C adatoms.

After achieving a critical diameter of semi-fullerene embryo, further growth continues as capped CNT growth. In the case of a smooth Ni(111) substrate, the critical diameter is ~0.8-0.9 nm. Since we have used 2D periodic models of CNT-Ni interconnects, they describe growth of SW CNT bundles containing nanotubes of *identical* chirality. Parameters of CNT bundles measured experimentally or simulated theoretically [2]. At any case, appearance of carbon pentagons upon a smooth nickel (111) substrate demands certain energy supply.

On the other hand, a presence of Ni nanoclusters as well as other structural defects on a smooth substrate makes unlikely growth of smooth graphene monolayer since the curvature of carbon adlayer clearly indicates a presence of both hexagons and pentagons from C atoms. Thus, the nano-structured Ni(111) substrate is a good catalyst for growth of both capped carbon nanotubes and fullerenes. The calculated bonding energies between CNTs growing on smooth and nanostructured Ni substrates differ substantially, thus confirming noticeably larger stability of the latter CNT-Ni contacts.

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