

Chapter 1

Adsorption and Doping as Methods for the Electronic Regulation Properties of Carbon Nanotubes

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Abstract This chapter contains general information about the doping of carbon nanotubes, which allows the reader better understand the main problem addressed in the book. It examines the interaction of gas molecules with the graphene lattice, discusses the differences between physical and chemical adsorption, as well as the differences between chemical adsorption and doping.

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Carbon nanotubes (CNT) are worthy of special attention from researchers and developers of modern electronic devices [1, 2] for their unique mechanical, electrical, and optical properties, which they exhibit in numerous experiments and applications [1]. They have branched surfaces (achieving hundreds of square meters per gram), that define their high sorption ability [2, 3], allowing CNT to adsorb great amounts of inert gases, hydrogen, metals, water, etc. Studies of adsorption process reveal their nature and characteristic parameters and is now one of most significant problems facing nanotechnology in general [4, 5]. Another important problem of CNT is connected with capillary phenomena, when the various substances are “drawn in” to the tubes [6]. This effects their study both theoretically [7] and experimentally [8–10]. This is important not only as an investigation of theses interesting objects, but also as an instrument of nanotube electrical property control and regulation.

Single-wall carbon nanotube (SWNT) properties depend on both their structure and morphology (chiral vector, length, diameter, the presence of closed or open ends, defects, etc.). The method of growing CNTs with certain and planned

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architectures should allow access to tubes with the required properties. Note, that the technique of growing CNTs and their refinement is permanently improving. Perhaps this problem will be solved in near future, although even now we can influence the growth of SWNT structures. We have effective methods, allowing the introduction of defects into CNT [11], to open the closed ends and cuts the tubes, decreasing their length [12–14].

It is sufficiently difficult to divide doping and adsorption processes for CNTs, because the CNT (just as the graphene plane itself) presents a continuous and entire surface. Therefore, the usual doping notion (an introducing of an admixture into the substance) is not applicable. We must initially define a special notion known as “CNT doping” as a process, when an admixture atom substitutes the basic atom in a carbon network node. This definition is near to the common doping notion, but is also near to the notion of “chemisorption”, when an admixture atom creates chemical bonds with the basic substance atoms, located at a surface. Nevertheless, we consider that the adsorption process includes all processes where a foreign atom interacts with a carbon network surface, but does not substitute the lattice atom.

It seems likely that in the CNT case it is impossible to use the notion of free charge carrier concentration to assess the results of doping. For example, oxygen adsorption favors the whole concentration growth in nanotubes, but oxygen does not replace the lattice carbon atoms and does not even form any chemical bonds with these atoms [2, 15, 16]. This is because the oxygen interaction with a CNT is a typical example of physical adsorption, which cannot change the CNT conductance. It is connected with the fact that CNTs under adsorption change their electron structure and consequently their main corresponding properties [17, 18].

The studies and understanding of these processes, as well as development of adequate mathematical models can form a grounding for new perspective technologies, allowing the production of new devices on CNT bases. The adsorption and doping processes are now the main tools for CNT property control and regulation.

Doping and encapsulation. In classic microelectronics for material electronic properties, doping is used (i.e., an impurity atom is introduced into the sample volume). The impurity atoms introduced into the CNT arrays can occur in the graphene lattice or occupy the inter-wall channels, thus we name it “volume doping”. For the SWNT the problem of doping is more complicated, because the SWNT presents a graphite sheet, being rolled up into a cylinder, i.e., into a continuous surface. We can consider an impurity introduced into the hollow nanotube inner space as “volume doping”, i.e., for SWNT this encapsulation process can be considered as a variant of volume doping. Moreover, the usual substitution doping, when one carbon network atom is replaced by an admixture atom, must be considered and named as “surface doping”.

Doping and adsorption. The doping affects on the electronic structure and the conductance of nanotubes but this influence dose not exclude the others local methods of CNT electronic property modification. We can change the structure and the conductance of SWNT by adsorption of any atoms. Adsorption can have a physical or chemical nature (chemisorption). For example, some experiments are

demonstrating that even weak physical adsorption of oxygen and nitrogen on a CNT can change their conductance. Chemisorption with the formation of an adsorbent new covalent or ionic bond with a nanotube is a more powerful tool for influencing SWNT properties. Even hydrogen (which in a physically adsorbed state practically has no influence on CNT conductance) in a chemisorbed state sufficiently affects their resistance. Chemisorption influence on tube conductance is comparable with a doping influence, but can be more easily realized practically.

Doping and chemisorption. The separation of chemisorption and adsorption for SWNT seems to be a conditional one. In both cases are formed some new chemical bonds between the adsorbed atom and the nanotube carbon network. As this takes place, so proceeds a sufficient change of the systems' electronic spectra and properties, as well as charge transport. For example, for nitrogen doping on SWNT we have two well-known doping mechanisms with near energy parameters: first, classical substitution (graphite-type) doping; second, pyridine-type doping. The chemisorption of the impurity atoms can be realized on both external and internal surfaces of a nanotube, and the case of internal chemisorption can be considered as volumetric adsorption.

The adsorption can have an accentuated applied meaning, for example, as a process allowing the design of hydrogen storage. The first investigation of CNT adsorptive abilities in respect to hydrogen gave very optimistic results. For example, Dillon obtained a value of 5–10 wt% [19], Chen obtained 10–20 wt% [20], whilst in other work [21–24] values of more than 8 wt% at 80 K and 10 MPa have been achieved. Note also, that the physical adsorption efficiency is connected with tube curvature [25] and an intensive adsorption runs into the tubes and pores, formed by tube bunches [21, 26–28], not considering the defect influence [22, 29].

The adsorption process plays an important role in the mechanisms of charge carrier transfer or carrier emission, and therefore the adsorption parameters must be defined to create any controlling technologies. The main method used to define these parameters are studies of the adsorption process kinetics, and particularly the gravimetric measurements under desorption. To obtain a definition of the adsorbed atoms or molecules energies and numbers it was first necessary to develop a general thermodynamic model of adsorption. In this book, such a model is generated on the basis of the Gibbs free energy minimization method studies [30–32]. The foundations of our calculation are described in several publications [33, 34].

The adsorption processes on carbon nanotubes have some important peculiarities in comparison with the adsorption on a volume substance. First, the tubes are charged and therefore there can appear with strong electric fields at their ends. Second, the nanotube surface has strong inner elastic stresses. Moreover, in a multilayer CNT every tube has its own field of elastic stresses, which increase with a decrease in tube radius. Hence, the adsorption processes in single-wall and multi-wall nanotubes are different in their features and respectively this difference must be taken into account in theoretical models and calculation algorithms for the adsorption process parameters in these cases. In general, the CNTs in terms of their structure are placed between graphene and fullerene [1, 6].

A detailed review of CNT adsorption is presented in a survey by Eletzky [6]. Adsorption theoretical models have been developed by [35]. Calculations [15, 16] have shown that for any adsorption type, the forbidden zone width narrows, but this effect is weaker for physical adsorption case. At high adsorbate, concentrations appear at discrete levels, splitting off from corresponding zones, with their positions changing with changes in the adsorbate donor–acceptor properties and concentrations. It is obvious, that this situation affects the CNT optical and electric properties, and this effect can be used for practical purposes. Thus, adsorption changes the electronic properties of the “CNT–adsorbate” system, and this can be used to create various types of sensor.

The authors of one piece of research [36] obtained analogous results. In particular, they showed that under physical adsorption of the complex organic molecules there proceeds a localization of the charge carriers on CNT, which defines some change in the nano-conductor resistance. The energy spectrum depends on the molecular system rigidity. A crystallization of the coating leads to a step-wise rigidity change with a step-wise growth of CNT conductance. The theoretical calculations were affirmed by the results obtained by the molecular dynamics method [37]. The adsorbed addend can be movable ones [36], and it was affirmed by Monte-Carlo experiments.

From the scientific literature data we can conclude that at low temperatures (up to 150 K) the adsorption is mainly physical in character with stable bonds between carbon and adsorbent not being formed. The physical adsorption is usually caused by various natural forces (van der Waals interactions, electrostatic polarization, etc.), characterized by an absence of exchange interaction, peculiar to the chemisorption. Under physical adsorption processes of the molecule decomposition into atoms, along with their recharging, does not occur, hence we can neglect the electronic processes. Note, that hydrogen physical adsorption is observed at low temperatures (up to 80 K) and its content is no more than 1.2 wt% of hydrogen. Such a small value of physical adsorption is connected with the fact that chemical bonds are not forming.

Chemisorption is characterized by the formation of covalent or ionic bonds, as well as an adsorbate changing their charge. The adsorptive abilities of nanotubes increasing in this case, but the adsorption process itself is more complicated, because for chemical bond formation the adsorbate must overcome a potential barrier. If the adsorbate (i.e., as for the case of hydrogen) exists in a molecular form, it must be transformed in an atomic form. At the same time the forces holding the adsorbate in place are stronger under chemisorption, something which arises from the amount of adsorbed substance. These properties make chemisorption a prospective process for hydrogen energetics in general (i.e., for creating hydrogen storage devices with working temperatures, exceeding the room temperature).

Investigations of the graphite paramagnets [38] and adsorptive characteristics [39] have shown that the nature of bond hybridization is changing for the adsorbent atom, on which the adsorption proceeds: namely $sp^2\pi$ -hybridization transforms into s^2p^2 -hybridization. This means that one of the carbon σ -bonds is being torn apart, whilst the two free bonds join the two hydrogen atoms (formed after the molecule

dissociates). There are also suggestions of other mechanisms of CNT electric property change.

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