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CARBON NANOTUBES AND THEIR PROPERTIES IN THE COURSE IN NANOMATERIALS FOR ENGINEERING STUDENTS

The article describes the sequence of presentation of the basic concepts and achievements of nanotechnology, nanomaterials types, the core technologies of their formation, methods of investigation of nanostructures, the basic physical and chemical properties of nanomaterials, the latest advances in the use of nanomaterials and nanotechnologies in various branches of engineering.

In the lecture course, students are introduced to the basic concepts and ideas of nanotechnology and nanomaterials, their classification and basic properties, methods of nanostructures' forming.

In the theoretical material of the lecture course the latest achievements in the field of nanomaterials are considered with the focus on graphene, carbon nanotubes and fullerenes. All of these materials are constructed with carbon atoms. Listeners' attention is drawn to the fact that certain special arrangement of carbon atoms can drastically change the properties of the material if created with the specific arrangement of atoms. A necessary condition for such a review is appropriate schematic arrangement of atoms.

Lecture material is related to the latest developments in nanotechnology, and is divided into teaching units in line with some of the brightest main results obtained in such critical areas as nanotechnology: nanobiology, nanomaterials, nanochemistry, nano, nanoengineering, nanoelectronics, nanoenergetika, nanotechnology safety.

Key words*: nanotechnology, nanotube, nanostructure, fulluren, engineering education.*

A course in nanotechnology and nanomaterials is now systematically read for engineering students attaining a master degree at Donetsk national technical university. The aim of the course is to give central concepts and ideas of nanotechnology, show various kinds of nanomaterials and their classification, study their specific physical and chemical properties, and also the most important methods of their fabrication and investigation.

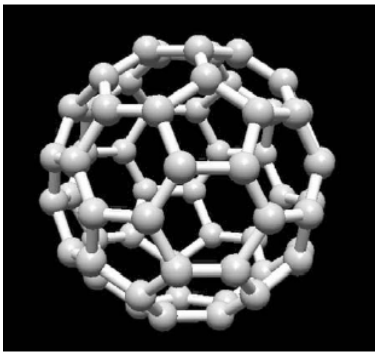


Figure 1. Bucky ball: C60 molecule (computer simulation)

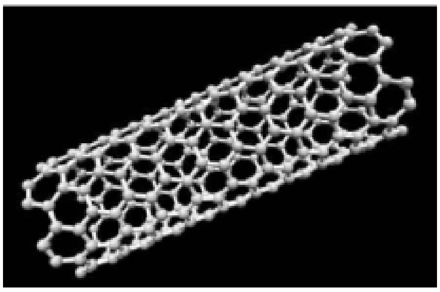


Figure 2. Graphite sheet wrapped into a cylinder to form a carbon nanotube (CNT)

A special interest among nanomaterials belongs to such carbon materials as fullerenes, graphene and nanotubes. The students' interest is drawn to the fact that all these materials are formed from only one element.

Carbon nanotubes (CNTs) were discovered in 1991 by Sumio Ijima of the NEC laboratory in Tsukuba, Japan, during highresolution transmission electron microscopy (TEM) observation of soot generated from the electrical discharge between two carbon electrodes. The discovery was accidental, although it would not have been possible without Ijima's excellent microscopist skills and expertise. What Ijima was, in fact, studying were C_{60} molecules, also known as *buckminster fullerenes*, previously discovered by Harold Kroto and Richard Smalley during the 1970s. Kroto and Smalley found that under the right arc-discharge conditions, carbon atoms would self-assemble spontaneously into molecules of specific shapes, such as the C_{60} molecule (see Figure 1).

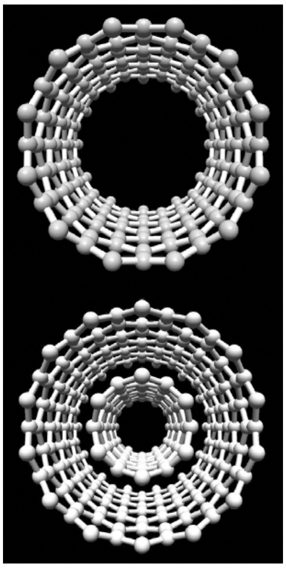


Figure 3. Single-walled and multiwalled carbon nanotubes

However, as shown by Ijima's discovery, under different experimental conditions, carbon atoms can instead self-assemble into CNTs.

CNTs are cylindrical molecules with a diameter ranging from 1 nm to a few nanometers and length up to a few micrometers. Their structure consists of a graphite sheet wrapped into a cylinder (see Figure 2). Depending on the processing conditions, CNTs can be either single-walled or multiwalled (see Figure 3).

Single-walled nanotubes (SWNTs) may be metallic or semiconductor, depending on the orientation of the hexagonal network with respect to the nanotube long axis, a property known as *chirality*. In particular, CNTs can be classified by a chiral vector, given by

$$C = na + mb$$

where a and b are unit vectors and n, m are chiral vector numbers that characterize the orientation of the hexagons in a corresponding graphene sheet (see Figure 4). In this configuration, the magnitude of the chiral vector C is the circumference of the nanotube, and its direction relative to the unit vector a is the chiral angle θ_0. The translation vector T defines the nanotube unit cell length, which is thus perpendicular to C. These parameters describe the way in which the graphite sheets are rolled up to form a tube structure. In this regard, three types of CNTs are possible: armchair, zigzag, or chiral (see Figure 5). An armchair nanotube is formed when $n = m$. In Figure 5 this occurs when the green atom matches the blue atom. The zigzag nanotube forms when $m = 0$ (the green atom matches the red atom).

The chiral type occurs when the chiral vector numbers (n, m) can assume any integer values and the chiral angle is intermediate between 0 and 30 (Figure 5). Among these three different types, armchair SWCNTs are metals, those with $n-m = k$ (k is an integer) are semiconductors with a small band gap, and the remainder are semiconductors with a band gap that is inversely proportional to the CNT diameter.

Carbon nanotubes exhibit various unique properties, such as the ability to withstand large stresses with little elastic deformation (Young's modulus = 1000 GPa), the capacity to endure enormous tensile stresses (30 GPa), and the aptitude of exhibiting superior current densities (10^9A/cm^2) and thermal conductivity (6000 W/mK). These two latter properties are due to the nearly 1-D electronic structure in metallic SWNTs and multiwalled nanotubes (MWNTs), which leads to ballistic transport, and the ease by which phonons propagate along the nanotube, respectively.

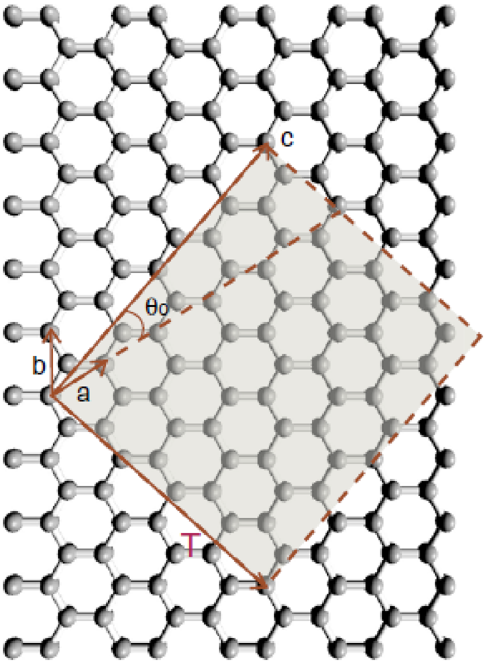
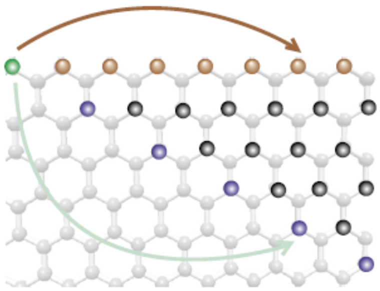
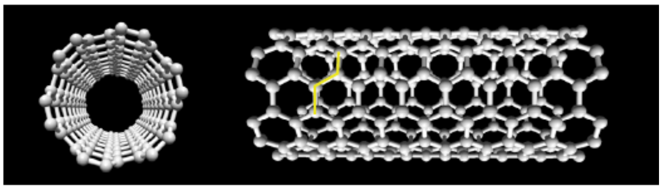
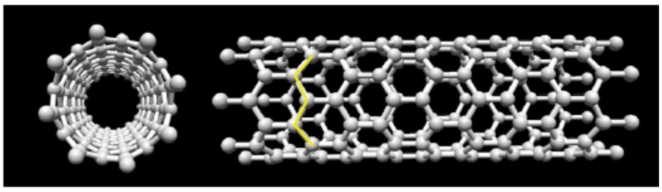


Figure 4. Graphene sheet rolled into a cylinder described by unit vectors a and b, chiral angle θ0, chiral vector C, and translation vector T. The figure represents a (4,2) nanotube, where the shaded area is one unit cell. (Adapted from Barry J. Cox and James Hill, University of Wollongong, Australia)

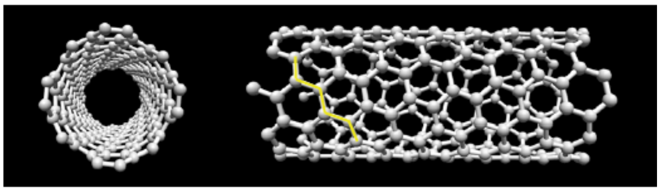




Armchair



Zig-zag



Chiral

Figure 5. Chirality in nanotubes, describing the way in which the graphite sheets are rolled up to form a particular tube structure.

So far, researchers around the world have been devising several methodologies to synthesize carbon nanotubes. The most common methods are the arc-discharge technique and chemical vapor deposition. These methods have seen significant improvements over the years, but they still suffer from (1) low yield, (2) very high cost, (3) difficulty in tuning the diameter of the nanotubes, and (4) difficulty in producing a single type of CNT without impurities. Table 1 shows some of the advantages and disadvantages of these current methods.

Table 1. Advantages and Disadvantages of Widely Used Techniques to Synthesize CNTs

Method	Type of Nanotubes	Diameter	Length	Advantages	Disadvantages
Laser vaporization	SWNT	1-2 nm	-	Few defects, good size control	Very expensive
Arc discharge	SWNT/MWNT	0.6-1.4 nm/10 nm	Short	Easy to produce, few defects	Random sizes, short length
CVD	SWNT/MWNT	0.6-4 nm/10-240 nm	Long	Easy to produce	Usualy MWNT, defects

Although these techniques have been the subject of considerable research, there are still many questions with respect to the processing variables that may condition the formation and growth of CNTs. Some noteworthy parameters that seem to affect the production of CNTs are temperature, pressure, and the type of catalyst used. As an alternative to the methods shown in Table 1, one other route for generating CNTs that could become promising in the near future is the process of metal dusting. Simply, metal dusting is the disintegration of metallic alloys by corrosion, which is initiated by exposure of pure metals or metallic alloys to strongly carburizing atmospheres. The result of the decomposition is a mixture of metal particles and carbon nanostructures. The great advantages of this catalytic route are that carbon nanotubes can be produced at moderate temperatures (around 650–750°C) in large volumes as well as low cost and their structure can be tailored by the catalytic properties of the metal or alloy selected. However, this method still requires further investigation».

Analyzing the structure of fullerene molecules, it is interesting to mention the analogy with filigree building constructions by the American R.B.Fuller. Such spherical molecules have much free space inside and may serve as reservoirs for various purposes, e.g. reservoirs of hydrogen molecules, which is very interesting in energetics.

However, these methods may dissolve some of the CNTs, cause structural damage to CNTs, or be unable to remove large particle aggregates. In addition, these purity-driven techniques tend to be very expensive.

Nevertheless, due to these outstanding properties, carbon nanotubes are likely to play a vital role in various areas, such as nanocomposites, nanoelectronics, hydrogen storage, field emission devices, and nanosensors. The area of nanocomposites is perhaps the first area where CNTs will have a commercial impact. Due to the outstanding modulus and tensile strength resulting from the covalent bonds between the carbon atoms, CNTs are one of the strongest materials known. In addition, CNTs exhibit a high aspect ratio. Therefore, CNTs are ideal as a reinforcement phase. In recent years, good progress has been made in developing CNT-based nanocomposites. In fact, several investigations have shown important enhancements in mechanical, electrical, and thermal properties of nanocomposite materials. However, significant challenges still remain—for example, tailoring the uniformity of dispersion within the matrix, controlling the alignment of CNTs, and making sure that there is a good interfacial bond between the CNTs and the matrix. Furthermore, due to the high cost of CNTs, particularly of pure SWCNTs, the addition of CNTs has been restricted to about 5% in weight.».

Specifically, the U.S. Department of Energy (DOE) has set the technological benchmark to 6.5 wt% (ratio of hydrogen to storage material). Currently, these hydrogen levels can be achieved by using gaseous and liquid hydrogen.

However, gaseous hydrogen occupies large volumes, whereas liquid hydrogen requires cryogenic containers, which drastically increase the system's overall cost. Solid-state hydrogen is thus the most promising route for hydrogen storage. Several publications have reported very high hydrogen storage capabilities in CNTs, ranging from 10 wt% to less than 0.1 wt% (see Figure 6). These experiments have been performed at ambient pressure and temperature, high pressure and room temperature, and cryogenic temperature.

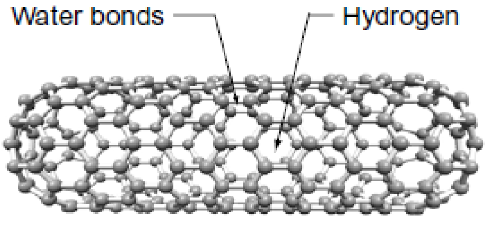


Figure 6. Carbon nanotubes (CNTs) for hydrogen storage

However, many of these experiments have been difficult to reproduce. This has been attributed to several factors, such as a large variation in the type and purity of CNTs tested as well as some difficulties in the characterization procedure. In addition, the mechanisms of hydrogen adsorption and the nature of chemical interaction have not yet been understood. Although some researchers claim that the major portion of hydrogen absorption is due to trapping sites, namely dangling bonds, with energies between 4.4 eV and 2.3 eV, depending on the trapping site, others argue that hydrogen trapping sites in carbon-related materials are either a result of physisorption (0.1 eV) or chemisorption (2–3 eV). Currently, the number of hydrogen trapping sites available under normal conditions is not sufficient to fulfill the goals set by DOE».

The material of the lecture about contemporary achievments of nanotechnology should be divided into didactic units in accordance with bright results in such important fields as nanobiology, nanoelectronics, nanoenergetics, nanotechnology for safety etc.

«In the area of nanoelectronics, CNTs have been sought as the new generation of interconnect structures as well as field-effect transistors.

Interconnects, which carry the electrical signals between transistors, are currently made of copper, but as electronic circuits continue to shrink, copper interconnects will suffer from overheating.

Conventional metal wires can typically exhibit current densities of 10^5 A/cm^2 until resistive heating becomes a problem. On the other hand, because of the nearly one-dimensional electronic structure of CNTs, electronic transport in metallic SWNTs occurs ballistically along the nanotube length, allowing the conduction of high currents with no heating. In fact, current densities up to 10^9 A/cm^2 have been observed in SWCNTs. This is because the electronic states are confined in the directions perpendicular to the tube axis. As a result, the remaining conduction path occurs along the tube axis. Due to the lack of phonon and/or impurity scattering perpendicular to the tube, CNTs behave as 1-D ballistic conductors.

Field-effect transistors (FETs), a type of transistor used for weaksignal amplification, are currently made from silicon. However, these devices are still a few hundred nanometers in size. The use of CNTs with sizes less than 1 nanometer in diameter would allow more of these switches to be part of a chip. In an FET, the current flows through a CNT with semiconductor properties along a path called the *channel*. At one side of the channel is a gold electrode called the *source*; at the other side of the channel is a gold electrode called the *drain* (see Figure 7). When a small voltage is applied to the silicon substrate, which acts as a gate in FETs, the conductivity of the CNT can change by more than a million times, allowing a FET to amplify a signal. Still in the area of nanoelectronics, a more challenging idea is to build entire electronic circuits out of CNTs, making use of their metallic and semiconducting properties. In this case, semiconducting CNTs are aligned on an insulator substrate, whereas metallic CNTs are placed above in close proximity to the bottom layer. By controlling the current, the top CNTs can be made to contact the bottom CNTs, producing a metal-semiconductor junction that acts as a switch.

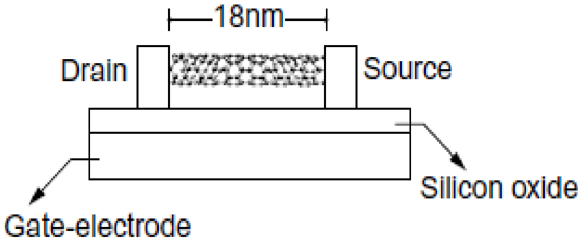


Figure 7. Typical field-effect transistor (FET)

Another application for CNTs is in the area of fuel cells and batteries, both for storage purposes. In the case of fuel cells, CNTs have been sought to store hydrogen, particularly for automotive applications, where hydrogen should be contained in small volumes and weights, yet enabling reasonable driving distances (500 Km).

Another area in which CNTs can potentially be of great interest is the field of supercapacitors. This is because CNTs exhibit high porosity, large specific surface area, high electrical conductivity, and chemical stability. In a conventional capacitor, energy is typically stored by the transfer of electrons from one metal electrode to another metal electrode separated by an electronically insulating material. The capacitance depends on the separation distance and the dielectric material inserted between electrodes. In the case of a supercapacitor, there is instead an electrical double layer (see Figure 8). Each layer contains a highly porous electrode suspended within an electrolyte. An applied potential on the positive electrode attracts the negative ions in the electrolyte, whereas the potential on the negative electrode attracts the positive ions. A dielectric material between the two electrodes prevents the charges from crossing between the two electrodes. If the electrodes are made of CNTs, the effective charge separation is about a nanometer, compared with separations on the order of micrometers for ordinary capacitors. This small separation, combined with a large surface area, is responsible for the high capacitance of these devices (one to two orders of magnitude higher than conventional capacitors). In addition, although it is an electrochemical device, no chemical reactions are involved, allowing the ultracapacitor to be rapidly charged and discharged hundreds of thousands of times. Supercapacitors employing multiwalled carbon nanotube electrodes have already achieved a capacitance ranging from 18 to 250 F/g.

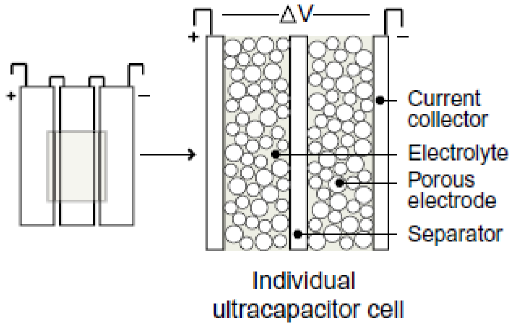


Figure 8. Schematic of a supercapacitor

Field emission is another area in which CNTs can prove particularly useful. As previously discussed, the concept of field emission involves the application of an electrical field along the CNT axis to induce the emission of electrons from the end of the tube. So far, the research has been directed toward using SWCNTs and MWCNTs for flat-panel displays and lamps. In the case of flat-panel displays, used in televisions and computer monitors, an electric field directs the field-emitted electrons from the cathode, where the CNTs are located, to the anode, where the electrons hit a phosphorus screen and emit light (see Figure 9). The area of flat-panel displays has attracted a good deal of attention from the industrial community, including Motorola and Samsung, which have produced several prototypes. Despite the potential market for this application, the current technology still suffers from several problems that are not easy to solve, such as the development of low-voltage phosphorus.

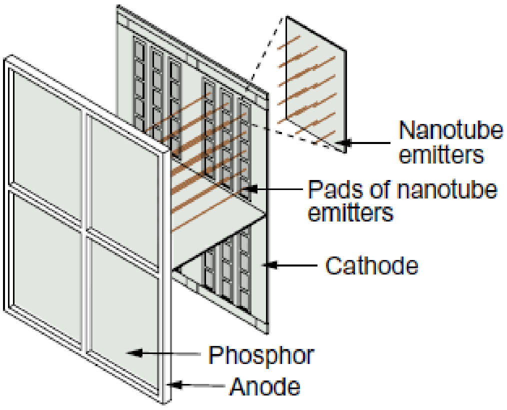


Figure 9. Flat-panel display

Obviously, once the technical problems are surpassed, the advantages of CNTs with respect to conventional liquid crystal displays are significant, in particular high brightness, a wide angle of view, and low power consumption. The technology for CNT-based lamps is imilar to the one used for flat-panel displays, comprising a front glass covered with the phosphor coating and a back cathode glass that includes the CNTs. CNT-based lamps are attractive because they are mercury-free while maintaining high efficiency and long lifetime».

After considerations of another obvious cases from various branches of nanoscience and technology the lecturer gives to students quite complete general picture of present-day achievements in nanotechnology.

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Е.И.Волкова, В.В.Приседский УГЛЕРОДНЫЕ НАНОТРУБКИ И ИХ СВОЙСТВА В КУРСЕ «НАНОМАТЕРИАЛЫ» ДЛЯ СТУДЕНТОВ ИНЖЕНЕРНЫХ СПЕЦИАЛЬНОСТЕЙ

В статье изложена последовательность представления основных понятий и достижений нанотехнологии, видов наноматериалов, основных технологий их формирования, методов исследования наноструктур, основных физических и химических свойств наноматериалов, современных достижений в применении наноматериалов и нанотехнологий в различных отраслях техники.

В лекционном курсе студенты знакомятся с основными понятиями и представлениями нанотехнологии и наноматериалов, классификацией и их основными свойствами, методами формирования наноструктур.

В теоретическом материале лекционного курса при рассмотрении современных достижений в области наноматериалов, в первую очередь, основное внимание обращено на графен, углеродные нанотрубки и фуллерены. Все эти материалы созданы на основе атомов углерода. Внимание слушателей обращено на то, что определенное специальное расположение атомов углерода позволяет коренным образом изменить свойства материала, созданного с таким расположением атомов. Необходимым условием такого рассмотрения является схематическое изображение соответствующих расположений атомов.

Материал лекции, связанной с современными достижениями нанотехнологий, разбит на дидактические единицы в соответствие с некоторыми, наиболее яркими основными результатами, полученными в таких важнейших отраслях нанотехнологий как: нанобиология, наноматериалы, нанохимия, наномедицина, наноинженерия, наноэлектроника, наноэнергетика, нанотехнологии для безопасности.

Ключевые слова: *нанотехнология, нанотрубка, наноструктура, фуллерен, инженерное образование.*

О.І.Волкова, В.В.Приседський ВУГЛЕЦЕВІ НАНОТРУБКИ ТА ЇХ ВЛАСТИВОСТІ В КУРСІ «НАНОМАТЕРІАЛИ» ДЛЯ СТУДЕНТІВ ІНЖЕНЕРНИХ СПЕЦІАЛЬНОСТЕЙ

У статті викладена послідовність представлення основних понять і досягнень нанотехнології, видів наноматеріалів, основних технологій їх формування, методів дослідження наноструктур, основних фізичних і хімічних властивостей наноматеріалів, сучасних досягнень в застосуванні наноматеріалів і нанотехнологій у різних галузях техніки.

У лекційному курсі студенти знайомляться з основними поняттями та уявленнями нанотехнології і наноматеріалів, класифікацією та їх основними властивостями, методами формування наноструктур.

У теоретичному матеріалі лекційного курсу при розгляді сучасних досягнень в області наноматеріалів, в першу чергу, основна увага звернена на графен, вуглецеві нанотрубки і фулерени. Всі ці матеріали створені на основі атомів вуглецю. Увагу слухачів звернено на те, що певне спеціальне розташування атомів вуглецю дозволяє докорінно змінити властивості матеріалу, створеного з таким розташуванням атомів. Необхідною умовою такого розгляду є схематичне зображення відповідних розташувань атомів.

Матеріал лекції, пов'язаної з сучасними досягненнями нанотехнологій, розбитий на дидактичні одиниці у відповідності до деяких, найбільш яскравих основних результатів, отриманих в таких найважливіших галузях нанотехнологій як: нанобіології, наноматеріали, нанохімія, наномедицина, наноінженерія, наноелектроніка, наноенергетіка, нанотехнології для безпеки.

Ключові слова: *нанотехнологія, нанотрубка, наноструктура, фулерен, інженерна освіта.*

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