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Aerosol synthesis and applications of single-walled carbon nanotubes

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Abstract. Aerosol methods for the chemical synthesis of single-walled carbon nanotubes are considered. Characteristic features and advantages of these methods are indicated. The possibility of controlling the growth and vapour deposition processes of single-walled nanotubes are discussed. It is shown that nanotubes prepared by aerosol synthesis can be directly used in various fields of technology. The bibliography includes 171 references.

I. Introduction

Interest in studies of carbon nanotubes (CNTs) was initiated in 1991 by a publication of Iijima,[1] in which he described the structures of carbon nanotubes with two and more walls. In 1993, Iijima and Ichihashi[2] and, independently, Bethune *et al.*[3] published the results of their studies on synthesis of single-walled carbon nanotubes (SWCNTs). However studies of CNTs began long before these publications. Probably, they were prepared at the end of 19th century for the first time,[4] whereas the evidence of their tubular structure was only obtained in the middle of the 20th century when transmission electron microscopy became available.[5,6] Afterwards, many publications devoted to research works on CNTs and nanofibres appeared both in international and in Russian journals.[7–17] The synthesis of CNTs is considered as one of the most important achievements in the materials science over the past 50 years.[18]

Carbon nanotubes, especially SWCNTs, possess unique mechanical, thermal and electrical properties.[19–21] Single-walled carbon nanotubes are the most durable of known materials, their Young modulus is exceptionally high.[22,23] Their high thermal conductivity is of large importance for many practical applications. Synthesis of CNTs with both semiconducting and metallic properties is feasible, their capability to sustain high electric currents represents an important feature, finding its use in micro- and nanoelectronics in manufacture of high speed transistors, memory elements, sensors, switches and also as conductors in integrated circuits. Composite materials based on CNTs are acquiring a wide spread at present. Nanotubes embedded in a matrix change composite thermal and electrical conductivity, as well as its optical and mechanical properties.[24–27]

The methods for the synthesis of CNTs can be classified according to the ways of carbon atomization as physical and chemical, being based on catalytic decomposition of carbon containing compounds.

The physical methods for the CNT synthesis consist in sublimation and subsequent desublimation of graphite and utilize arc discharge, laser irradiation or inductive heating.[3,28,29] Their major disadvantages are high energy consumption for the sublimation, necessity to use low pressure, low product yield, relatively high cost of the carbon source (graphite), difficulties in automation and realization in the industrial scale. In addition, nanotubes prepared by sublimation – desublimation are typically tangled in the form of bundles, therefore they have to be separated and purified by chemical methods.

The chemical methods for the CNT synthesis are based on catalytic decomposition of carbon precursors. Their obvious advantage is the growing of the carbon nanotubes at relatively low temperatures ($\sim$600 – 1000 °C). Two methods can be distinguished among the chemical methods, those are the methods with the use of substrate supported catalyst[30–32] and floating catalyst.[33–35] In the first method, the process of precursor decomposition and growth of CNTs occurs on the catalyst applied on the substrate

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surface. Oxidized single crystalline silicon,[36] fused silica,[37] graphite,[38] as well as compounds with extended surface like SiO_2,[39] MgO,[40,41] Al_2O_3,[42] $CaCO_3$,[43] zeolites[44] can serve as the substrate. In the floating catalyst method, CNTs grow on the surface of particles floating in a gas, *i.e.* on aerosol particles, therefore this method is often called aerosol.

Transition metals Fe, Ni and Co are usually employed as catalysts. Their role comes down to accumulation of carbon and its segregation as CNTs or nanofibres and is determined by the ready solubility of carbon in these metals. Promoting agents are utilized in many processes along with the catalysts. For example, small additions of sulfur or sulfur containing compounds (thiophene or hydrogen sulfide),[45–51] and also of phosphorus containing compounds (triphenylphosphine)[52] can significantly increase the yield of nanocarbon materials. Lately some works were published (see, for instance, Refs 53–56), indicating possibility to use as catalysts not only Au, Cu and Ag, which can hardly be conceived in this role earlier because of limited solubility of carbon in them, but also other elements and compounds: Pd, Pt, Mn, Mo, Cr, Sn, Mg, Al, Si, SiC, Ge, Al_2O_3. In many cases catalytic activity of particles is determined by their size or their specific treatment immediately before the synthesis. In addition, it was shown that CNTs can grow even without metallic catalyst,[57–60] the smallest splinters of the support and particles of silicon oxide originating under mechanical action on the support and from atomic layer deposition (ALD), respectively, serve as catalysts. Diamond nanoparticles were also successfully used as catalyst, SWCNTs obtained in this way do not contain any element except carbon.[59]

The most often used sources of carbon in the chemical synthesis are methane, acetylene, ethanol, ethylene and carbon monoxide.[45,61–66] Almost any compound containing carbon can be utilized in the CNT synthesis. Particularly, organic polymers, natural organic compounds like camphor derivatives, terpentine and eucalyptus oils, and also coal, kerosene, liquefied petroleum gas, natural and coal gases were successfully tested.[45,67–69]

The chemical vapour deposition method is one of the most promising methods for the synthesis of CNTs under controlled conditions. Depending on the pursued aim, the following types of the CNT production can be distinguished:

— the large-scale synthesis of CNTs with their subsequent purification for further use in various practical applications;

— the synthesis of CNTs of pre-defined purity and specified morphology for their direct application.

Each of these types of syntheses has its specific features. The first approach is facilitated by well-developed methods of CNT purification. In addition, functionalization of CNTs makes it possible to disperse them into water or organic media for their subsequent use, and particularly, for their introduction into composites. In recent years, methods for the separation of CNTs according to their properties (metallic or semiconducting) were developed,[70,71] as well as those for the isolation of nanotubes of a specified chirality.[72,73] Undoubtedly, large-scale manufacturing will determine the fields of the CNT application, requiring the large-scale utilization of CNTs (first of all, in composites) and being presently restricted by high cost and low accessibility of the nanomaterials.

During the production of CNTs according to the second approach, the intermediate stages between the synthesis of nanotubes and their use are minimized. In the framework of industrial production this means the synthesis on a support or aerosol synthesis with subsequent deposition on or transfer to a support, on which CNTs will be used. This makes it possible to avoid laborious steps of purification of CNTs from a catalyst and substrate and dispersing of CNTs in solvents before their deposition on a desired support. The aerosol synthesis giving relatively pure SWCNTs of high quality in the continious mode is the most preferable for this approach.

It is worth noting that sufficient level of purity of CNTs is determined by their particular application and is not necessarily 100%. Catalytic particles encapsulated in carbon nanotubes have often no effect on CNT properties and in some cases can even improve properties important for some applications. For example, based on our experience, we can assert that 2 at.%–8 at.% impurity of iron encapsulated in carbon nanotubes has no appreciable effect on electrical and optical properties of SWCNT films.

An important feature of the aerosol synthesis is a possibility of direct deposition and transfer of SWCNTs from a filter, on which they precipitate from the gas phase, to almost any surface by pressing the filter to the support under heating (the thermo-compression)[74] or at room temperature (the dry transfer method).[75] Additional advantages of this synthesis consist in possibility of continuous control of the quality of CNTs, of their characteristics (like diameter and even chirality) and morphology (for instance, production of SWCNT bundles coiled or orderly packed), as well as feasibility of separation of individual SWCNTs from their bundles in the gas phase.

Despite the large number of publications devoted to CNTs both in international[29,45,61,76–80] and in Russian[62–64,66,81–88] journals, the aerosol chemical synthesis remains without due attention. Primarily, this can be explained by relative complexity of this method. The aerosol synthesis requires exact adherence to the experimental conditions as the processes of the carbon precursor decomposition and CNT growth in the gas phase occur fast (in seconds). In this review it is attempted to summarize published data on the methods for aerosol synthesis of carbon nanotubes and subsequent applications of CNTs in high-technology fields like electronics, optics and electrochemistry.

II. Methods for the aerosol synthesis

One of the most popular methods for the synthesis of SWCNTs is based on thermal decomposition of hydrocarbon vapours (generally, mixed with the thiophene vapours). This method was used by Oberlin *et al.*[89] in the 1970s. Almost all later works represent developments of the methods for the carbon fibre synthesis elaborated by Endo.[90]

The first reports on aerosol synthesis of SWCNTs appeared in the late 1990s. The chemical synthesis of SWCNTs using a flow of the mixture of benzene, ferrocene and thiophene heated to 1100–1200 °C was proposed by Cheng *et al.*[46,91] in 1998. Aproximately at the same time SWCNTs were prepared by pyrolysis of C_2H_2 with the use of iron pentacarbonyl and metallocenes of the iron group

elements.[92,93] The synthesis of multi-walled CNTs by the method of floating catalyst was carried out by Ci *et al.*[52,94] However, the product was collected from the reactor walls, but not from the gas phase in all of these works.

There are a lot of works where aerosols are utilized. However, not all of them are related to the aerosol synthesis because the CNT growth often proceeds not on the surface of floating particles, but on the reactor walls or on supports positioned in the reactor.[94–99] Usually, such syntheses are carried out during pre-specified time and the processes are not continuous as it is in the aerosol method. Sometimes the aerosol form is used only to feed the carbon precursor and catalyst into the reactor. Aerosol can be produced by microwave generator or by various sprayers, as well as by ionization in the electric field. All such methods are called aerosol-assisted methods.

The first true chemical method for the aerosol synthesis was HiPco (High Pressure carbon monooxide) process established in 1999 by Nikolaev (Rice University, Houston, USA),[100,101] who worked in the group of R E Smally, the 1996 Nobel Prize Laureate in Chemistry. It was one of the first chemical methods, which made it possible to obtain SWCNTs in gram quantities.[102] The method is based on catalytic disproportionation of CO on the surface of iron catalyst particles according to the following reaction equation

$$2\,CO \rightleftharpoons CO_2 + C(solid),\quad \Delta H = -169\ kJ\ mol^{-1} \qquad (1)$$

under high (up to 50 bar) pressure (Fig. 1 *a*).[100] Vapour of $Fe(CO)_5$, a catalyst precursor, is introduced into the reactor with a cold flow of CO and is mixed in turbulent regime with hot CO. The synthesized SWCNTs are collected by filtration of the flow in the cold part of the reactor. Gaseous CO_2 is removed by passing the flow through molecular sieves. Purified gaseous CO is compressed and supplied back to the reactor. Recycling of CO is required because of its low decomposition degree. As a rule, the mole fraction of CO_2 at the reactor outlet does not exceed 0.005%. The HiPco process makes it possible to obtain SWCNTs of 97% purity in yield of $\sim$500 mg h^{-1} (Ref. 102). The seventh generation of such reactors operates at Rice University at present, they differ from the previous reactors by the geo-

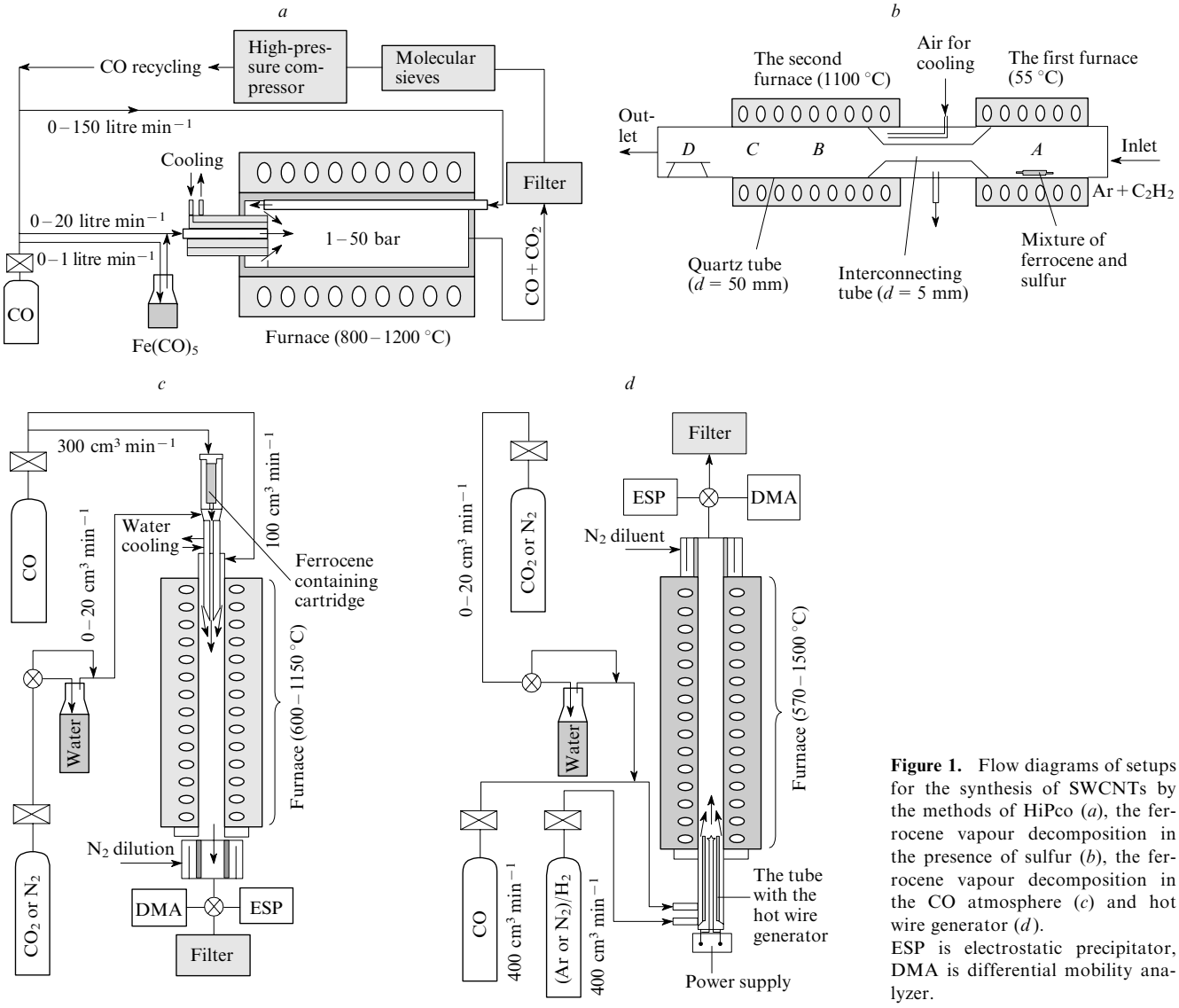


Figure 1. Flow diagrams of setups for the synthesis of SWCNTs by the methods of HiPco (*a*), the ferrocene vapour decomposition in the presence of sulfur (*b*), the ferrocene vapour decomposition in the CO atmosphere (*c*) and hot wire generator (*d*).
ESP is electrostatic precipitator, DMA is differential mobility analyzer.

metries of the inlet and flow mixing, and also by heat exchanger design.

Approximately a year after publication of the first paper devoted to the HiPco-method, Bladh *et al.*[34] published their results on the disproportionation of CO in the temperature range 700–1000 °C under atmospheric pressure in the presence of small amounts of acetylene and hydrogen. Later, a prototype of the HiPco apparatus was used for production of SWCNTs by thermal decomposition of ferrocene in argon atmosphere, *i.e.*, without any additional sources of carbon.[103]

Japanese researches[104, 105] developed the aerosol method for SWCNT synthesis based on the use of catalytic iron particles in colloidal solution (in micellar form). The particles incorporated into hydrocarbon aerosol droplets are introduced into the hot reactor. This results in evaporation of the carbon source and growth of SWCNTs on the surface of catalytic particles. The method is called DIPS (Direct Injection Pyrolytic Synthesis).[47, 104–106] Later on, the catalytic particles were substituted by their precursor, ferrocene.[107, 108] It was shown in studies of the effect of aromatic hydrocarbons on the final product that the best sources of carbon are aromatic hydrocarbons containing substituents with sp^2-hybridized carbon atoms like styrene, allylbenzene and divinylbenzene.[107]

The group of Windle[48, 109–111] from the University of Cambridge developed a method based on decomposition of vapours obtained by evaporation of ethanol (or hydrocarbons) with dissolved ferrocene. They succeeded in preparation of tangled nanotubes suitable for continuous twisting into threads consisting of single-, double- and multi-walled nanotubes. An analogous method was used in other works.[112, 113] The company 'NanoComp' (USA) used a similar method for the manufacturing of thick films and threads from SWCNTs, which are utilized in production of reinforced or conducting composite materials.[114]

It is worth noting that the synthesis of CNTs in flames containing precursors of carbon and catalysts can be attributed to the aerosol methods also. A series of works devoted to the flame syntheses of multi-walled and single-walled CNTs has been published.[115–121] In this method, fuel mixtures containing carbon in excess relative to oxygen (2–3 times higher than the stoichiometric ratio) are used. A part of the fuel is expended for heating of the reaction mixture in the combustion regime, whereas the rest is used as the reagent. Hydrocarbons (methane, acetylene, ethylene, propane) are usually utilized as carbon sources and metallocenes or metal vapours are used as the catalyst precursors. Particular methods can differ by supply mode of the fuel, the oxidant (with prior mixing or without it) or catalyst precursor. SWCNTs obtained in flames are usually free from amorphous carbon, but contain significant amounts of oxidized catalyst and therefore their chemical purification is necessary.

An analogous problem also arises in the other chemical method for CNT synthesis: spray pyrolysis with formation of solid particles on which CNTs grow.[97, 121–123] Aqueous solutions of metal salts (for example, iron or aluminium nitrates) are used in this synthesis, they are sprayed and introduced into a first furnace to evaporate water and to pyrolyse the residue to form metal oxides. To remove water vapour, the aerosol is passed over silica gel. Then the obtained particles together with acetylene and hydrogen enter a second reactor heated to higher temperature, where the CNT growth occurs. Only multi-walled CNTs are synthezed by this method yet.

Synthesis of SWCNTs from a ferrocene–sulfur–acetylene mixture was carried out for the first time by the group of Xie[33, 50, 51, 124–127] from the Institute of Physics of Chinese Academy of Sciences. The flow diagram of the experimental setup is shown in Fig. 1*b*.[125] The mixture of powdered ferrocene and sulfur is sublimed in the first furnace (zone *A*) at 55 °C and is carried by the flow of argon with acetylene at a flow rate of 300–2000 $cm^3\ min^{-1}$ through thin pipe to the second furnace. The mole fraction of acetylene in the flow is 0.05%–0.3%. The temperature in the second reactor (zone *B*) is 1100 °C. The precursors are decomposed at this temperature, and single-walled[127] or two-walled[33, 50] CNT are formed, they are collected either from the reactor walls in the cold zone or from the support placed in zones *C* and *D*.

Afterwards the possibility of assembling rings of SWCNTs as shown in Fig. 2*a* was demonstrated.[128] With this aim the gas flow was artificially whirled in the reactor to form a circulation zone. The individual rings of SWCNTs were studied, their field emission and conductivity were examined. It was shown that ordered packing of SWCNTs from the gas phase on the support can be achieved under influence of the variable electric field between the electrodes. Fig. 2*b* shows SWCNTs ordered under variable field of strength of $\sim$10 kV cm^{-1} with frequency of 100 kHz. The capability to produce thin and thick films of randomly packed SWCNTs was also demonstrated.[126, 129]

In the case of the direct use of SWCNTs, it is very important to avoid formation of undesirable side-products like soot or amorphous carbon and to reduce the amount of catalyst. The content of the metal can be reduced by optimization of the synthesis. Formation of the non-graphite impurities can be decreased using an optimal concentration of the carbon source and utilizing CO as the source,

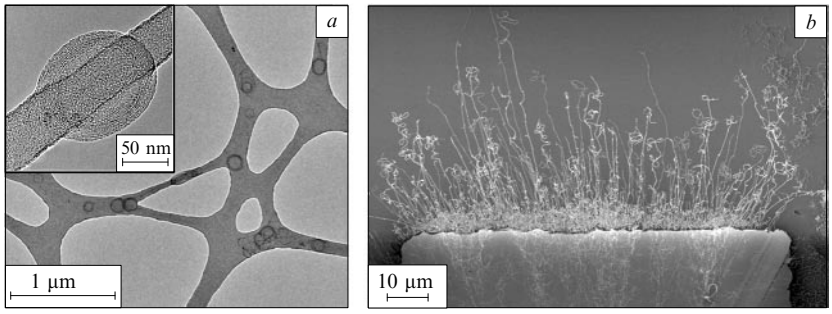


Figure 2. TEM image of SWCNT bundles twisted into coils in the gas phase (*a*) and SEM image of ordered SWCNTs deposited from the gas phase in ac electric field with the frequency of 100 kHz (*b*).

The results obtained for SWCNTs prepared by ferrocene vapour decomposition (Fig. 1*c*).

because the latter is known to decompose mainly on the catalyst surface. Carbon monoxide was successfully applied to control SWCNT growth in the aerosol synthesis. Particularly, two methods for synthesis of SWCNTs were realized based on ferrocene vapour decomposition [130] and use of hot wire generator methods.[35]

The experimental setup for the use of ferrocene vapour decomposition represents a vertical reactor, in which the laminar regime is maintained to control the growth of catalytic particles and SWCNTs (Fig. 1 *c*).[130] Ferrocene is evaporated at room temperature by passing CO (at a flow rate of 300 $cm^3\ min^{-1}$) through a cartridge filled with powdered ferrocene and silicon dioxide (as an inert filler). Through water cooled branch pipe the flow containing ferrocene vapour (with pressure of 0.8 Pa) enters a ceramic tube with the inner diameter of 22 mm, a zone of high temperatures, where it is mixed with additional flow of CO (flow rate is 100 $cm^3\ min^{-1}$). The outlet of the branch pipe (maintained at 24 °C) is located where the tube walls have temperature of ~700 °C, this ensures large temperature gradient necessary for fast heating of the gas mixture. The synthesised SWCNTs are collected by passing the flow through a filter (in the case of macroscopic studies) or an electric filter (for the subsequent studies by means of transmission or scanning electron microscopy).

Raman spectra of SWCNTs obtained with the use of lasers operating at 633 and 488 nm are shown in Fig. 3 *a*. The presence in the spectra of the radial breathing mode (RBM) in the low frequency region (~200 cm^{-1}) and *G*-mode of high intensity (with maximum at 1592 cm^{-1}) indicates the formation of SWCNTs. A special feature of the spectra is low intensity of *D*-mode (at ~1340 cm^{-1}), this indicates small portion of unordered carbon in the products of this synthesis. Metallic SWCNTs determine additional modes of Breit–Wigner–Fano lying close to *G*-bands (~1550 cm^{-1}).[131] The diameters (D_n/nm) of the nanotubes can be estimated from frequency of RBM (ν/cm^{-1}) using the equation

$$D_n = \frac{283}{\nu}.$$

The calculation showed that the diameters of the prepared nanotubes lie within 1.2–1.6 nm. Depending on the experimental conditions, the mean diameters of SWCNTs obtained in this way can vary from about 1 to 2 nm (Fig. 3 *b*).

The method based on the use of the hot wire makes it possible to synthesize both single-walled [35] and multi-walled CNTs.[132] In this method, the catalyst particle (iron, nickel) generation is carried out by evaporation from the hot wire. Subsequent cooling of the catalyst results in nucleation of the oversaturated vapours. Then, the catalytic particles enter the reactor, where they are mixed with a carbon source under atmospheric pressure. The diagram of the experimental setup used in this method is shown in Fig. 1 *d*.[35] The ceramic tube with inner diameter of 22 mm is placed inside the furnace. Thin iron wire of 0.25 mm in diameter is used for resistive heating, the wire is located in the ceramic tube with outer and inner diameters of 13 and 9 mm, respectively; the tube is placed in the reactor in the region of wall temperature of ~400 °C. Iron particles are brought into the reactor by flow of the $N_2 + H_2$ (or $Ar + H_2$) gas mixture with molar ratio 93:7 (flow rate is 400 $cm^3\ min^{-1}$) and are mixed with the outer flow of CO

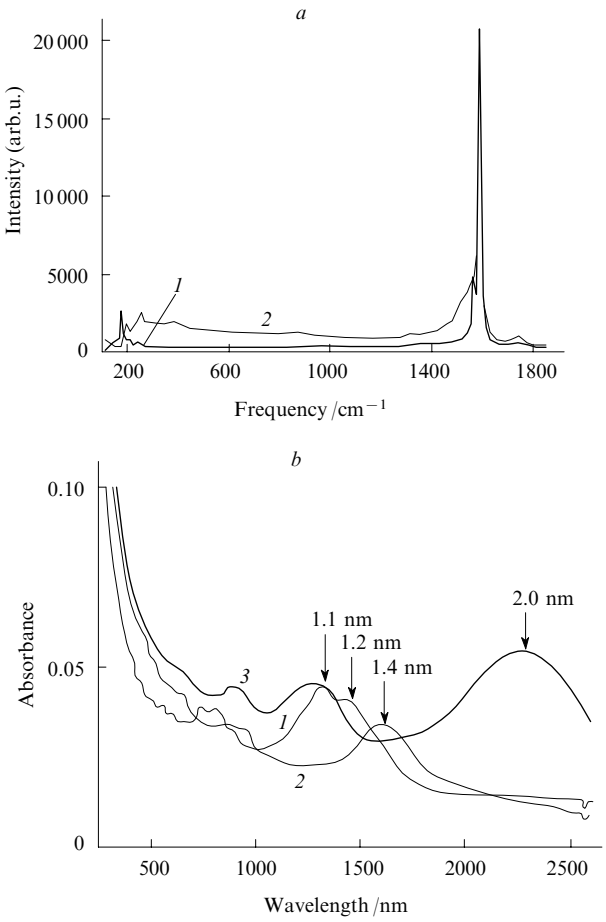


Figure 3. Results of studies of SWCNTs synthesized by ferrocene decomposition.
(*a*) Raman spectra obtained under laser excitation at 488 (*1*) and 633 nm (*2*); (*b*) absorption spectra of SWCNTs prepared using different amounts of carbon dioxide added (*1* for 0, *2* for 0.5%, *3* for 1.0%) at 890 °C. The mean diameters of SWCNTs calculated for electronic transitions E_{11} are shown above the arrows.

(400 $cm^3\ min^{-1}$). Inside the reactor, in addition to reaction (1), interaction of CO and H_2 occurs

$$CO + H_2 \rightleftharpoons H_2O + C(solid),\ \Delta H = -136\ kJ\ mol^{-1}. \qquad (2)$$

To prevent product deposition on the walls at the reactor outlet, the flow is uniformly diluted with nitrogen (12 litre min^{-1}) coming from porous tube. The mean residence time of the products in the reactor is ~2–3 s. An important feature of this process is high effectiveness of the use of the catalyst: practically all the catalyst particles initiate the SWCNTs growth. This is achieved by introduction of minor amounts of etching agents, usually, water vapours or carbon dioxide.[133]

In the course of the aerosol synthesis it is very important to control its conditions like the types of flow and mixing of gases, as well as to maintain the necessary temperature gradient. With this aim, we performed calculations of heat and mass transfer in the two reactors with the use of the Programme code 'StreamWise'.[134] An axisymmetric problem was solved numerically. Along with laws of conservation of mass, momentum and energy, the floatation effect was taken into account during the solution. The boundary

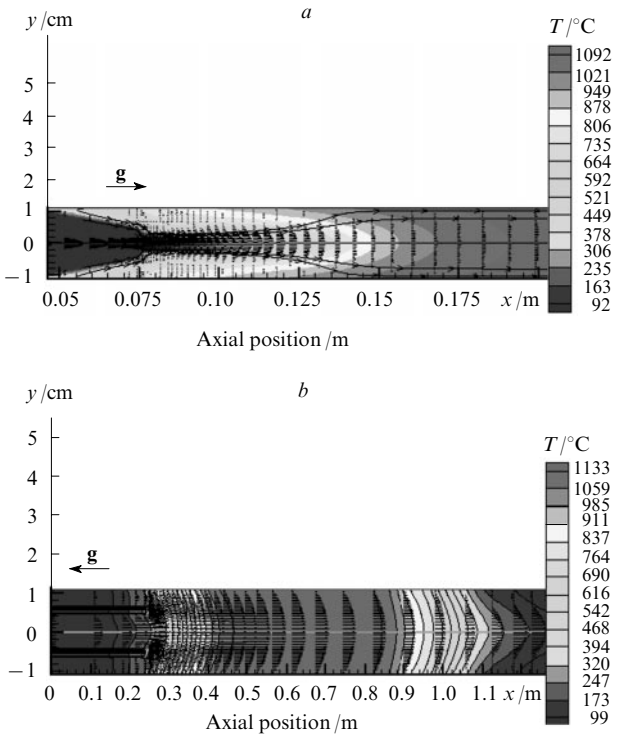


Figure 4. Results of calculations of heat and mass transfer in the reactor using ferrocene vapour decomposition in the CO atmosphere at 1150 °C (*a*)[130] and in the hot-filament reactor at 1200 °C (*b*);[35]
y is the radial coordinate corresponding to the distance from the reactor tube axis, *x* is the coordinate corresponding to the distance from the reactor inlet cross-section along the reactor axis, **g** is the gravity vector.

temperature conditions were taken from experimental data. The vectors of flow rates and temperature profiles are shown in Fig. 4. The flow in the reactors was laminar. The results of modelling of the heat and mass transfer at the reactor inlet are shown in Fig. 4 *a* for the ferrocene vapour decomposition process, assuming that the branch pipe is located 7.5 cm away from the inlet and the maximum temperature is 1150 °C. As can be seen, a zone of the flow circulation appears near the branch pipe, ferrocene vapours do not participate in this circulation according to the calculations. The maximum temperature in the reactor is reached in the middle of flow. The second reactor was modelled without consideration of the presence of the hot wire. It was found that under these conditions, the flows have no circulation in the heating zone and reach the wall temperature, thus determining favourable conditions for SWCNT growth.

III. Control and optimization of the aerosol synthesis

1. Continuous monitoring of the synthesis of the single-walled carbon nanotubes

Despite the significant progress in the synthesis of SWCNTs, the methods for their investigation and analysis are left immutable, those are electron microscopy and spectral methods like Raman spectroscopy and optical absorption. These methods enable us to characterise the material, but do not give instant information concerning the quality of the product prepared under given conditions. For continuous monitoring of the products and conditions of a process in the reactor, a differential mobility analyzer (DMA) can be used.[135–137]

Such analyzers are widely used to determine the particle size distribution.[138] The principle of its operation consists in differentiation of charged particles in aerosol by their mobility in the electric field and subsequent measurement of their concentration. The electric field is usually created between two cylindrical electrodes, the preselected potential is applied to the inner electrode, while the outer electrode is grounded (Fig. 5 *a*). Having entered the DMA, the aerosol

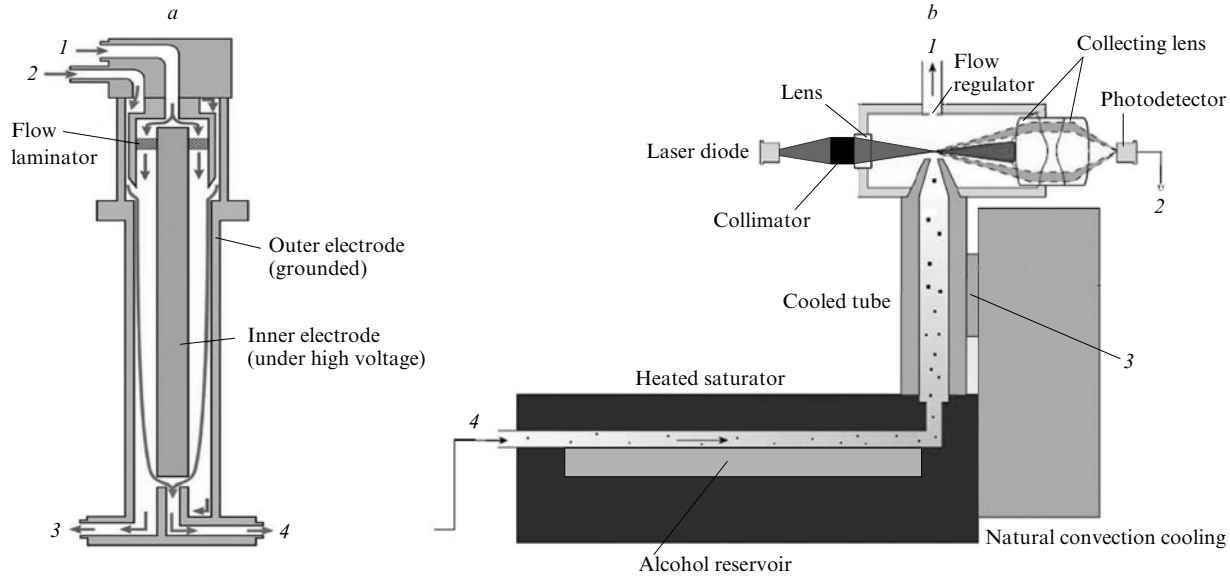


Figure 5. Diagrams of the differential mobility analyzer (*a*) and the condensation counter of aerosol particles (*b*).
(*a*) (*1*) The flowing gas supply, (*2*) polydisperse aerosol supply, (*3*) the excess gas outlet, (*4*) the monodisperse aerosol outlet;
(*b*) (*1*) pumping out, (*2*) the electrical pulse output, (*3*) thermoelectric heating transfer, (*4*) the aerosol inlet.

particles move with the flowing gas and deviate by the Coulomb forces toward the inner electrode having a narrow gap at its bottom for extraction of the particles of specified mobility. Then these particles are directed to an aerosol counter of particles or to a Faraday cell to measure their concentration or the total charge of the particles of the given mobility, respectively. The measurement of voltage on the inner electrode makes it possible to scan particle size in the range determined by the regulated gas flow, the voltage and the DMA geometry. Radioactive source or corona discharge is usually used to charge the aerosol particles before they enter the DMA.

A condensation particle counter is capable to measure concentration of particles with size of >3 nm in the range from 0 to 10^7 particles in 1 cm^3. First, the aerosol flow passes through the heated saturator, where butanol is evaporated. Then, the aerosol mixed with butanol vapour comes to a cooled tube, where the vapour becomes supersaturated and condenses on the aerosol particles. This leads to growth of the particles to micrometre size and such particles are detected optically. In the case of relatively low concentrations, the optical detector counts separate pulses produced by each particle (droplet) moving through the sensitive area. When the concentrations are high (10^4-10^7 particles per cm^3), the instrument switches to photometric regime of operation, when the concentration is associated with the scattered light intensity.

An example of size distribution of the aerosol particles when the product consists of either inactive catalyst particles or SWCNTs is illustrated by Fig. 6. Clear difference in the particle distributions upon conditions favourable and unfavourable for the nanotube growth is seen. On going from unfavourable to favourable conditions of growth, the total concentration of the aerosol particles decreases 2–5-fold, as a rule, whereas the mean DMA diameter shifts to larger values.

The considered methods make it possible to control the product yield in the continuous regime and significantly facilitate experiments on search for optimal conditions of the synthesis. It is worth to note that the mean DMA diameters (100 and 35 nm) corresponding to SWCNT growth in the reactors using ferrocene vapour decomposition and the hot wire do not supply direct information concerning the length or diameter of the prepared nanotubes. However, the measured DMA diameters and, accordingly, mobility in the electric field can be correlated with real geometries of SWCNTs (or their bundles) having specific aspect ratio ($\beta = L/D$).[135]

Kim *et al.*[137] used this approach to determine conditions for the synthesis of carbon fibres in the gas phase. A model of Brownian motion of oblong objects in the electric field was suggested.[139] On the basis of this model, it was shown that orientation of the objects is chaotic if the strength of the electric field is low (<1 kV cm^{-1}) and the values β are small (<30). The carbon nanotubes should orient along the electric field with increase of these quantities.

A method for determining the kinetic parameters of carbon fibre growth in the gas phase from the measured DMA diameters of the fibres synthesized at different temperatures was suggested.[140] It was ascertained that the energy barrier to the limiting stage of the fibre growth is ~ 80 kJ mol^{-1}. The combined use of DMA measurements of mobility and mass of the aerosol particles was suggested for determination of the CNTs and fibre density.[141] Such approach gave possibility for reliable determination of the fibre density (1.74 g cm^{-3}).

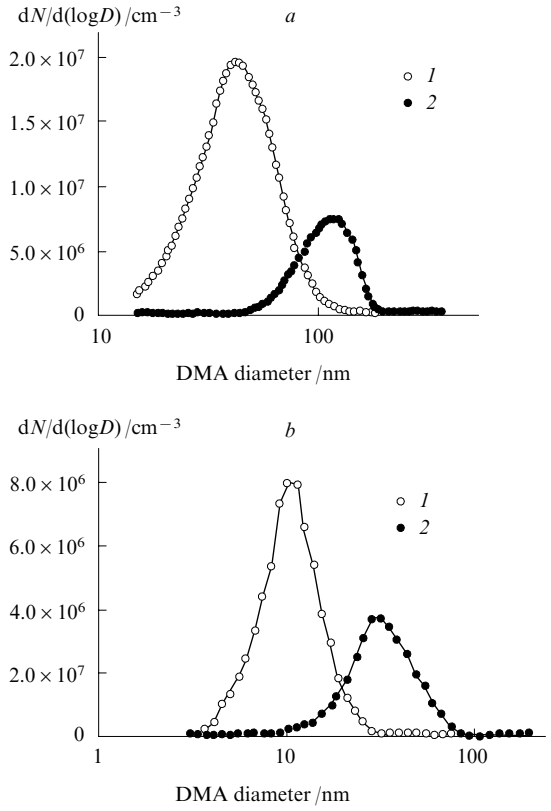


Figure 6. Particle size distribution under conditions, when either SWCNTs or inactive catalysis particles are formed in the reactor using ferrocene vapour decomposition (*a*) or the hot wire generator reactor (*b*) upon the passage of different gases.[135]
(*a*) (*1*) N_2, (*2*) CO; (*b*): (*1*) N_2, (*2*) mixture of H_2 and N_2. *N* is the number of particles in the volume unit.

Baron *et al.*[142, 143] developed dielectrophoretic method for measurement of size of asbestos and glass fibres and separation of the fibres by their size in the range 5–50 microns in alternating electric field. An anomalous behaviour of DMA during measurement of the aerosol flow containing SWCNTs or carbon fibres was reported.[144] At high electric field an electrical breakdown occurred in DMA, it could be explained by orientation of SWCNTs in the gas phase along the electric field. An analogous effect was also observed by us during measurements of SWCNTs prepared in the reactor using ferrocene vapour decomposition.

The aerosol methods of study can also be used for monitoring the CNT synthesis with the use of a supported catalyst.[145] It was shown that CNT growth in the system methane–hydrogen on nickel particles supported on silicon is accompanied by formation of aerosol, the size of the aerosol particles can be used to judge the development of the process.

2. The methods for deposition of single-walled carbon nanotubes

The simplest way of collection of CNTs prepared in the gas phase is filtration of the flow. Fig. 7 shows SWCNTs deposited by filtration through nitrocellulose disk filters of

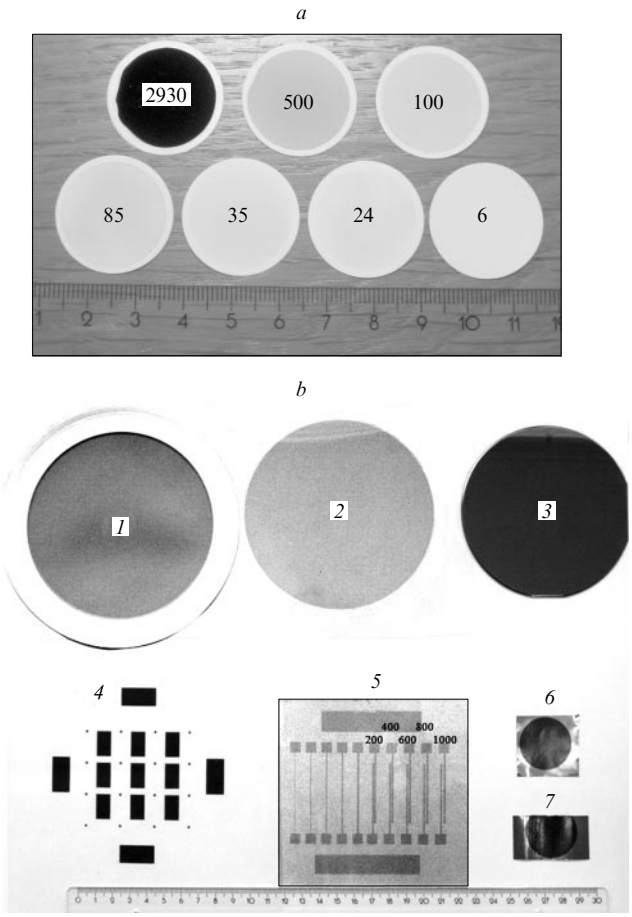


Figure 7. Photographies of films of SWCNTs collected on nitrocellulose filters (*a*), the filter with deposited SWCNTs and different supports, on which the nanotubes were transferred by the dry transfer method (*b*).[75]
(*a*) The numbers show film thickness in nm; (*b*) (*1*) filter; (*2*) the polyethylene terephthalate (PET) support; (*3*) the silicon plate completely covered by SWCNTs; (*4*, *5*) the SWCNTs applied with the use of masks placed under the filter and transferred to PET (the distance between electrodes is shown in μm); (*6*, *7*) the iron and copper foils, respectively, on which SWCNTs were transferred.

2.45 cm in diameter (Millipore Corporation, USA) at the reactor outlet. The SWCNT film thickness varies from a few to thousands of nanometres depending on deposition time.

Deposition of SWCNTs from the gas phase can also be carried out with the use of thermostatic precipitator (TP).[146] The principle of operation of TP is based on the theromophoresis phenomenon consisting in that the aerosol particle travelling in a high-gradient temperature field moves from the hot to cold zone.[147] The diagram of TP is shown in Fig. 8 *a*. The aerosol flow in this device moves through a spacing (of 0.55 mm) between two plates, the upper of which is resistively heated to 120 °C, while the lower one is cooled by running water to 10 °C. The support for deposition of nanotubes is fastened on the cold plate. A significant advantage of the particle collection with the use of TP consists in possibility of utilization of supports of any types. In addition, high uniformity of deposits of nanometre-scale particles is achieved on areas of millimetre-scale.[146]

Both neutral and charged SWCNTs can be deposited from the gas phase on a support at room temperature using of point-to-plane electrostatic precipitator (In-Tox Products, USA). In this apparatus, SWCNTs are ionized on moving through corona discharge. This rises the current between the needle-like electrode and the grounded plate, and SWCNTs charged in the corona discharge are deposited on the support surface by electrostatic forces (Fig. 8 *b*).

Charged SWCNTs can also be collected on a support to which a certain potential is applied (Fig. 8 *c*). This type of electrostatic precipitator (ESP) represents a cylindrical chamber with an inner horizontally situated metallic electrode close to which the support is located.[148] A constant negative (or positive) electrostatic potential is applied to the inner electrode, while the outer part of the construction is grounded. To ensure the most effective deposition, the electric field of $\sim 2-5$ kV cm^{-1} is utilized. This method allows one to achieve low density distribution of SWCNTs (close to the electric conductivity threshold, *i.e.*, of $\sim 1-5$ bundles of SWCNTs per square micron).[149] The density of deposited SWCNTs, which is determined by the deposition time, can be estimated from decrease of the particle concentration using a counter connected to the ESP output.

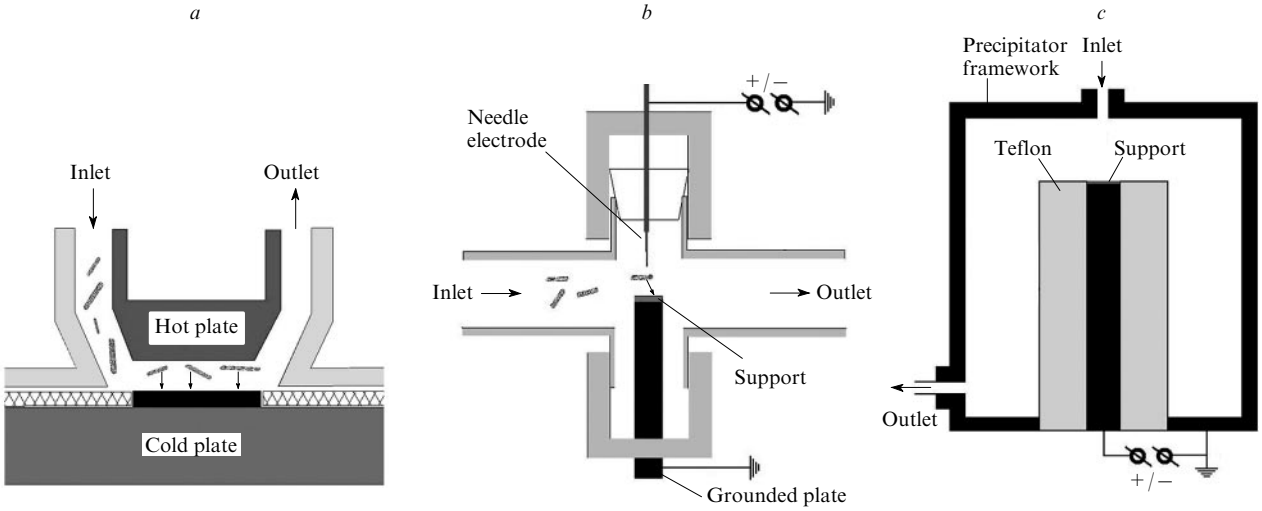


Figure 8. Diagrams showing the operating principles of different precipitators.
(*a*) The thermophoretic precipitator;[146] (*b*) the point-to-plane electrostatic precipitator for collection of both charged and neutral aerosol particles;[147] (*c*) the cylindrical electrostatic precipitator for collection of charged particles of a particular polarity.[148]

3. Methods for separation of the single-walled carbon nanotubes

Individual SWCNTs of specified chirality and orientation can be of considerable interest for many practical applications. With the use of the individual SWCNTs one can create field-effect transistors, memory devices, gas sensors and quantum wire, they can also be used as light sources. Therefore the methods for synthesis of the individual SWCNTs are highly needed. However the problem of fabrication of devices based on individual SWCNTs is very complicated at present because the process of manipulation of nanometre-scale objects is very time-consuming. In addition, due to van der Waals interaction CNTs spontaneously assemble into bundles upon contact; therefore most of methods for the CNT synthesis do not give the individual nanotubes. Additional laborious operations like ultrasonic treatment, functionalization, or addition of surfactants are usually required to separate bundles into individual nanotubes. However, shortening of SWCNTs occurs upon ultrasonic treatment as it is necessary to use very high energy to separate bundles into individual nanotubes. Functionalization results in undesirable changes in the electrical and optical properties of the nanotubes. Use of surfactants requires subsequent careful washing or another treatment to remove these substances. Individual CNTs can be synthesized on supports by chemical vapour deposition from the gas phase. However the necessity to use high temperatures (>400 °C) for the synthesis inevitably restricts the choice of materials for the support.

One-step process of separation and deposition of the individual SWCNTs prepared in the gas phase on various supports at room temperature is considered.[150] It is based on spontaneous charging of SWCNTs in the gas phase upon bundle formation. It is found that charged SWCNTs are gathered in bundles at the outlet of the reactor with hot wire, whereas electrically neutral nanotubes are individual. The SWCNT concentration in the gas phase can be controlled by changing the concentrations of catalyst and carbon source, which is carbon monoxide. The charged SWCNTs are removed from the flow by an electrostatic filter consisting of two parallel metallic plates 10 cm in length placed at 1 cm from each other with potential difference between them of $\sim 3-4$ kV. The remaining part of uncharged individual SWCNTs that has passed through the electrostatic filter is deposited by means of thermophoresis. Fig. 9 shows micrographs of SWCNTs collected at the reactor outlet before and after the removal of charged products from the flow. It is seen that this methods enables one to obtain individual nanotubes.

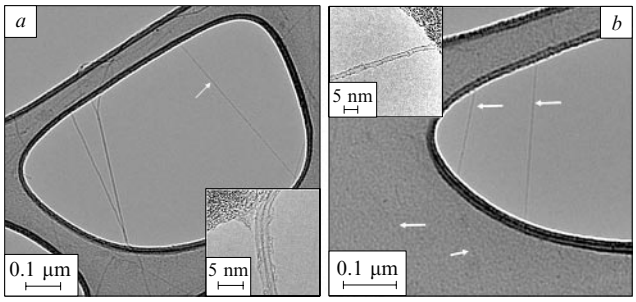


Figure 9. TEM images of SWCNTs collected just after the reactor (*a*) and after removal of charged particles from the flow (*b*).[150] Individual SWCNTs are indicated by arrows.

4. Influence of the synthesis conditions on characteristics of carbon nanotubes

Studies of SWCNT growth in the hot-filament reactors with the use of ferrocene vapours showed that the presence of small amounts of etching agents like CO_2 or H_2O vapours, forming on the reactor walls or deliberately introduced, are required for an effective synthesis.[133, 151, 152] The TEM images demonstrating effect from CO_2 and water vapour additives on the nanotube length are shown in Fig. 10. SWCNTs prepared without etching additives are of ~ 60 nm in length, whereas in the presence of CO_2 or water vapour, the length of the nanotubes exceeds 300 nm.

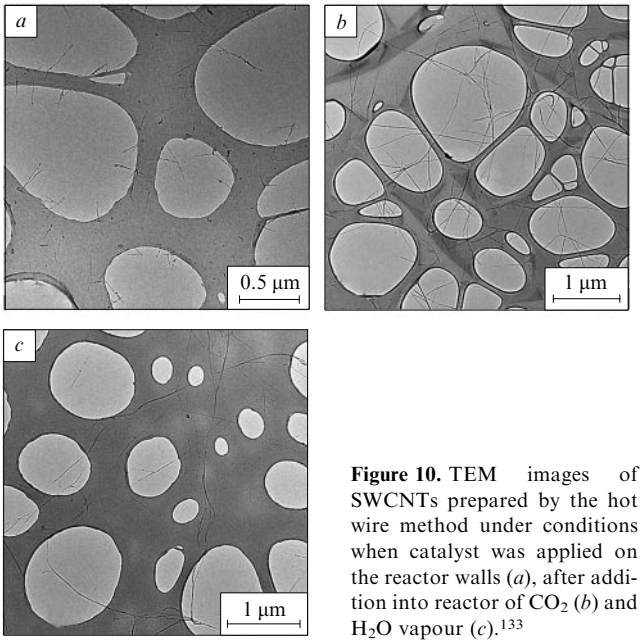


Figure 10. TEM images of SWCNTs prepared by the hot wire method under conditions when catalyst was applied on the reactor walls (*a*), after addition into reactor of CO_2 (*b*) and H_2O vapour (*c*).[133]

In addition, it was revealed that minor additives of the etching agents result in significant changes in the CNT diameters. As an example, Fig. 3 *b* shows absorption spectra of SWCNTs prepared in the reactor using ferrocene vapour decomposition at 890 °C in the presence of different amounts of CO_2. When no CO_2 is added, growth of SWCNTs with bimodal size distribution occurs (the mean diameters are equal to 1.1 and 1.2 nm). On addition of 0.5% and 1.0% of CO_2, the size of nanotubes increases to 1.4 and 2.0 nm, respectively.

Possibility to control products of the synthesis is demonstrated by Sato *et al.*[153] in the substrate-supported catalyst method and also by Kim and Zachariah[141] in the aerosol method. With this aim, the catalyst particles obtained by laser ablation of a nickel target and fritted in the gas phase were separated according to their mobility in the electric field. Then, Sato *et al.*[153] deposited the particles of 5 nm on a silicon support and synthesized thin multiwalled carbon nanotubes of similar size from the acetylene–argon mixture. Kim and Zachariah[141] introduced two isolated fractions of particles of 10 and 20 nm in size together with hydrogen and acetylene into the reactor, this

led to growth of fibres with close diameters in the gas phase. It is worth to note that the particle diameter usually exceeds the SWCNT diameter 1.4–1.6-fold when the hot-filament reactor is used and 2–3-fold for the reactor using ferrocene vapour decomposition.[154]

Chiang and Sankaran[155,156] investigated the possibility to change the chirality of SWCNTs in the aerosol method. With this aim, bimetallic (Ni/Fe) nanoparticles with narrow size distribution were prepared in a flow plasma reactor, their introduction into a furnace (at 600–700 °C) together with acetylene and hydrogen resulted in SWCNT growth. As it was shown, changes in composition of the catalyst particles and temperature affect the chirality of the prepared SWCNTs.[156]

5. Synthesis of nanobuds

By introduction of vapour of H_2O or CO_2 into the reactor, we succeeded in preparing SWCNTs coated with fullerenes and fullerene-like particles (Fig. 11). Later on, this material was called carbon nanobuds as fullerenes on the SWCNT surface resemble buds on the tree branches.[157,158] As it was shown, the optimal concentration of reactants introduced into the reactor using ferrocene vapour decomposition is from 45 to 245 ppm for H_2O and from 2000 to 6000 ppm for CO_2. Density functional theory calculations performed in the approximation of strong coupling demonstrated possibility of existence of fullerenes covalently bonded to SWCNTs via [2+2]- and [4+4]-cycloaddition, as well as possibility of formation of a united hybrid structure fullerene–SWCNT.

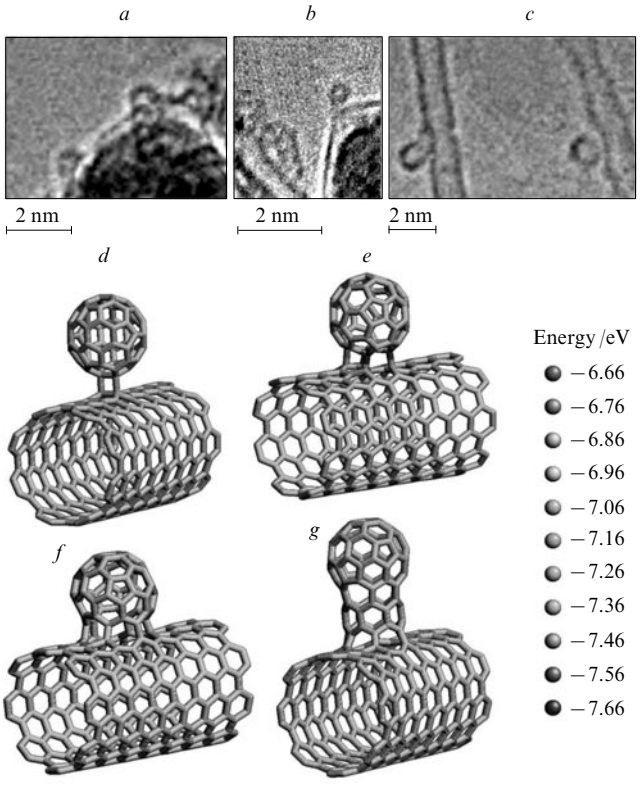


Figure 11. High-resolution TEM images of fullerenes on the surface of an iron particle (*a*), on carbon coating a catalyst particle (*b*), and of carbon nanobuds where fullerenes form the common structure with a nanotube and are attached to the nanotube surface (*c*).[157]
Results of numerical calculations performed in an approximation of strong coupling based on density functional theory show several scenarios of joining of fullerenes to SWCNTs: [2+2]- (*d*) and [4+4]-cycloaddition (*e*) and formation of the united hybrid structure (*f*, *g*). The binding energy is shown on the right side.

It is experimentally established that carbon nanobuds possess some properties exceeding the corresponding properties of non-bonded SWCNTs and fullerenes. For instance, the structure including fullerenes with strongly curved surface along with lengthy, chemically inert, but thermo- and electro conductive SWCNT showed very good capability to cold field electron emission.[157,158] Higher reactivity due to the presence of the fullerene fragments opens up new perspectives for functionalization. Fullerenes on the SWCNTs are supposed to be suitable for the use as molecular anchors preventing slipping of nanotubes in composites. In addition, it is expected that electrical and optical properties of the material can be changed or even tuned owing to the charge transfer between SWCNT and fullerene fragments.

IV. Applications of single-walled carbon nanotubes

The individual SWCNTs obtained by electrostatic separation of bundles were used for making high-performance field-effect transistors. It is well known, that the transistors based on SWCNTs are characterized by a very high mobility of charge carriers,[159] and typically have a large hysteresis in the dependence of current (I_{ds}) on the gate voltage (V_g). This hysteresis, undesirable for transistor operation, can be successfully used for creation of memory devices. A method for control of the memory effect in transistors fabricated on the basis of individual SWCNTs was earlier proposed,[160] it is based on the use of special materials of nanometre thickness as isolating layer of the gate (Fig. 12). Later, Rinkio *et al.*[161] demonstrated a memory element characterized by the shortest recording/erasing time of 100 ns and capable to endure more than 10 000 cycles, a layer of HfO_2 was utilized in this memory element as a gate dielectric and simultaneously as the outer layer protecting from the environment.

Devices based on the individual SWCNTs are of large scientific interest. However, fabrication of the devices from the individual CNTs represents a very complicated problem because of difficulties in manipulation of objects of nanometre scale. The complexity of positioning and attaining of the necessary orientation of the individual SWCNTs is a strong hindrance for mass production of the devices.[149] Electron-beam lithography and multistep processes of nanolithography should be used for this purpose. However, characteristics of a group of nanotubes forming a film rather than those of a single nanotube can be more important for some applications. In this case uniform properties of the SWCNT films will be achieved by statistical averaging of properties of individual nanotubes, comprising the film. This averaging results in reproducible behaviour on areas larger than single SWCNT size while properties of single SWCNTs depend on their chirality. Various devices and their parts created on the basis of SWCNT films are already known. For example, the group properties of nanotubes found their use in diodes, elements of logic circuits, solar batteries, displays and sensors.[162–167]

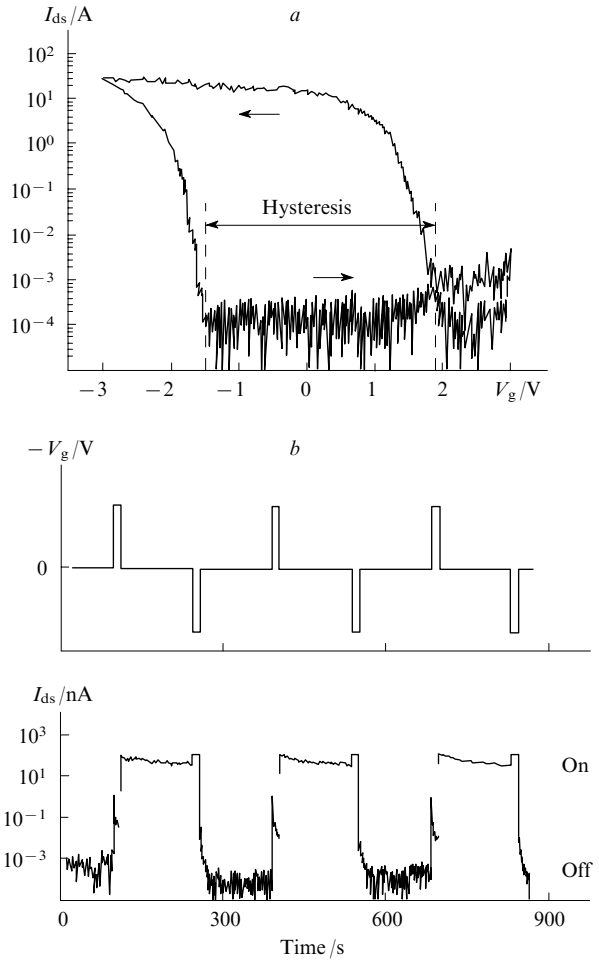


Figure 12. The dependence $I_{ds}-V_g$ for typical field-effect transistor fabricated using an individual semi-conducting SWCNT with thin gate dielectric layer of HfO_2 for excitation voltage of 10 mV between drain and source (*a*) and the memory effect illustration (*b*).[160]
(*a*) Hysteresis indicates different gate voltage on going from the negative to positive field and back; (*b*) The upper figure shows the gate potential change with time, the lower figure displays the corresponding gate current change; the transistor changes the state 'on' to 'off' when the positive gate voltage is changed for the negative voltage.

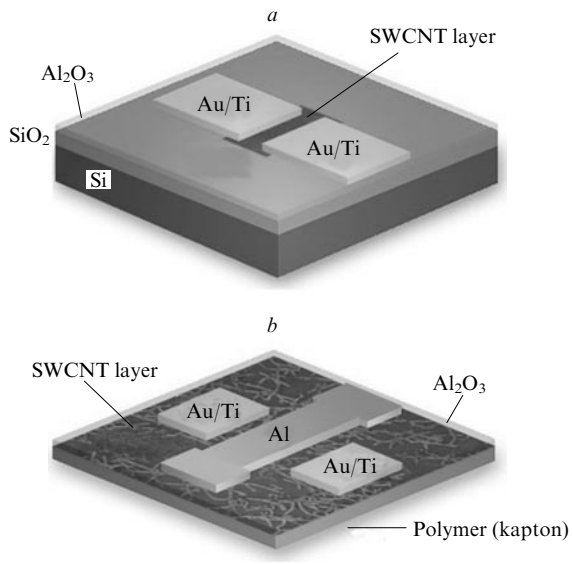


Figure 13. Schematic representation of field-effect transistors on silicon support (*a*) and on polymer (*b*).[149]
(*a*) The support is utilized as the lower gate separated from the nanotube layer by the dielectric (SiO_2) layer; the upper layer of Al_2O_3 grown by the method of layer-specific deposition of atomic layers is needed to isolate the device from outer exposures and to decrease the dependence $I_{ds}-V_g$ hysteresis; (*b*) Nanotubes are applied on polymer (kapton), the Ti/Au electrodes are applied on top; the upper aluminium gate is separated from the nanotube layer by thin layer of Al_2O_3.

By utilizing the aerosol reactor using ferrocene vapour decomposition, thin-film transistors on silicon and polymer supports were produced by standard photolithography methods (Fig. 13).[149] The transistors showed quite good characteristics (Fig. 14). Although the charge carrier mobility turned lower than in transistors fabricated on the basis of individual nanotubes, it exceeded mobility in thin-film transistors based on organic semiconductors by at least an order of magnitude. Afterwards, the parameters like ratio of turn-on and turn-off currents and mobility of charge carriers were significantly improved up to $\sim 10^7$ and 35 $cm^2\ V^{-1}\ s^{-1}$, respectively, by lengthening of nanotubes and changing the geometry of contacts between them. Calculation of the mobility using a more rigorous approach, taking into account areas occupied by nanotubes, gave the value of 634 $cm^2\ V^{-1}\ s^{-1}$ (Ref. 167). Nanotubes obtained in the aerosol synthesis were used to create a ring oscillator from 44 thin-film transistors and to produce transparent and flexible integrated circuits, including inverters, logic gates (NAND, NOR), RS-triggers and master-slave D-triggers.

Thicker SWCNT films have also many potential applications, for instance, as transparent electrodes. In the near future, such electrodes can replace tin-doped indium oxide (ITO) electrodes, which are extensively utilized in electronics. Contrary to ITO, SWCNTs can be used for the fabrication of flexible and cheap devices. A simple method based on thermo-compression was proposed [74] to integrate SWCNT films of adjustable thickness, transparency and conductivity into polymeric films. The obtained material showed excellent cold electron field emission properties.[74] Because the product collection is carried out at room temperature in the aerosol method, SWCNTs may be deposited or transferred from the filter to almost any material, including polymers sensitive to elevated temperature.[75] With this purpose, SWCNTs collected on a filter should just be pressed against the target support. It is possible because of weak adhesion of nanotubes to materials, employed for manufacturing of the filters. Flexible polymers like polyethylene terephthalate or polyethylene, as well as glass, quartz, silicon and various metals can serve as the supports. A synthesis of very durable transparent high-conductive SWCNT film on quartz reactor walls was reported.[126] This film may be taken off and transferred to any other support.

An interesting application is the use of films as optically transparent chemical electrodes. A unique combination of high conductivity, well-developed surface, low background current and electrocatalytic activity in many electrochemical reactions stimulated wide use of electrodes made of SWCNT films in electrochemistry. A simple and easily

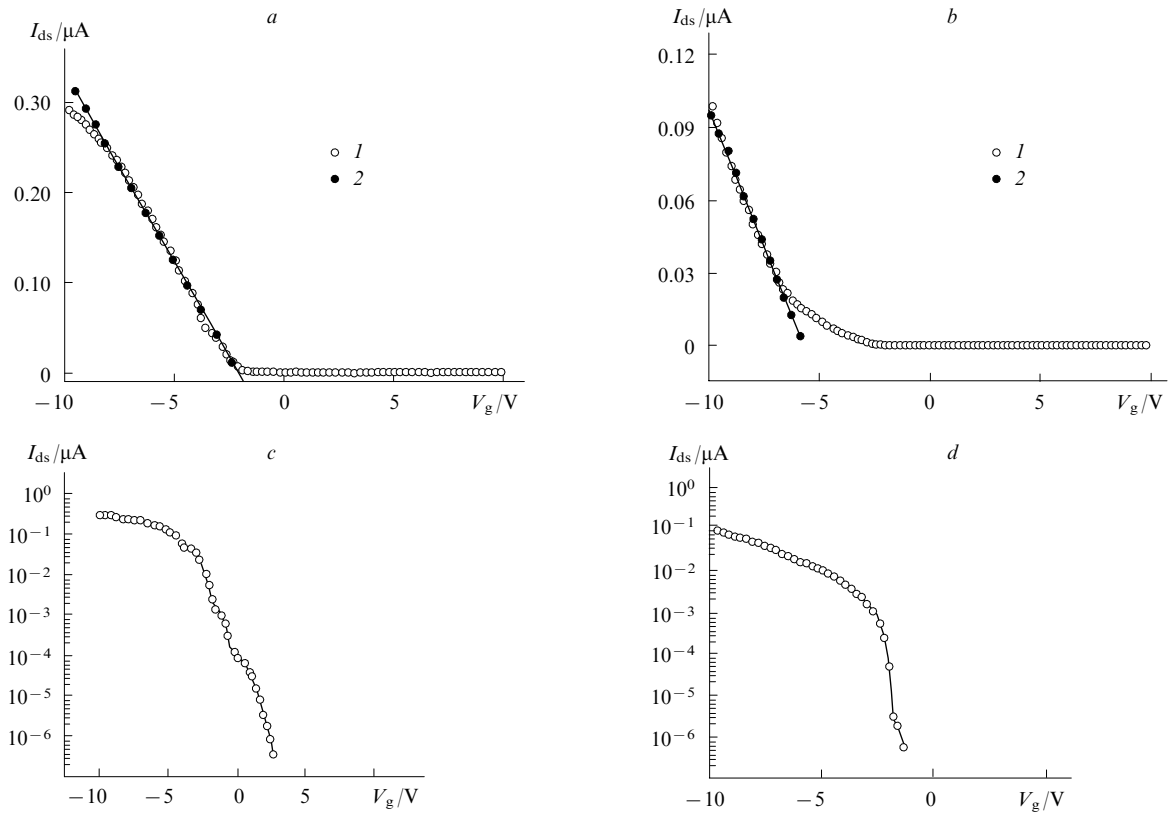


Figure 14. Dependencies $I_{ds} - V_g$ for transistors with lower (*a*, *c*) and upper (*b*, *d*) gates.[160]
(*a*) Both the distance between the electrodes and their width is 50 μm, the average density of the nanotube deposition is equal to ~2–3 bundles per 1 μm^2; (*b*) the distance between electrodes is 150 μm, their width is 200 μm; the charge carrier mobilities are 2–4 $cm^2\ V^{-1}\ s^{-1}$ at on/off current ratio of $> 10^5$ for both the transistors; (*1*) current–voltage characteristic, (*2*) the linear regime.

reproducible method for production of optically transparent electrodes from SWCNTs on flexible and transparent polyethylene terephthalate (PET) supports was reported.[168] The electrodes exhibited excellent electrochemical properties for a series of redox couples covering a wide potential window (Fig. 15).

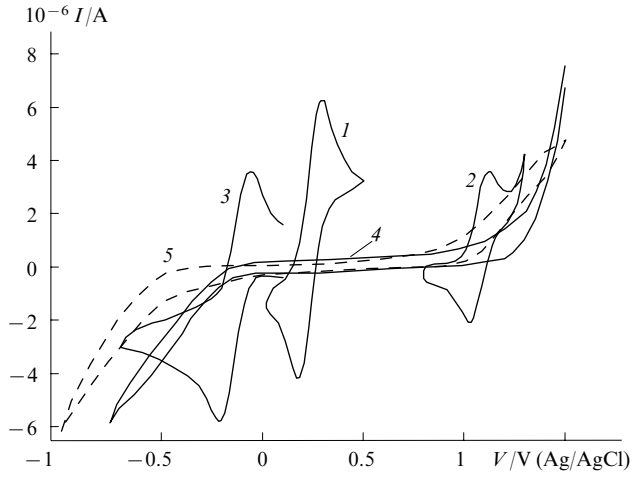


Figure 15. The current–voltage dependences obtained using optically transparent SWCNTs/PET electrode with transmittance coefficient of 92% at 550 nm.[168]
(*1*) Oxidation of 0.6 mM ferrocenemethanol in 0.1 M KCl, (*2*) oxidation of 1 mM $Ru(bipy)_3^{2+}$ in 0.2 M KNO_3, (*3*) reduction of 4.9 mM $Ru(NH_3)_6^{3+}$ in 0.5 M KNO_3, (*4*) the background noise level in aqueous solution of 0.2 M KNO_3, (*5*) the background noise level in 0.1 M $LiClO_4$ in acetonitrile. Scanning speed is 0.01 V s^{-1}.

An analogous method of dry transfer of the SWCNT film was applied to make SWCNT based saturable laser light absorber, which is utilized to modulate the laser quality factor. According to our data, this absorber exhibits the broadest operational bandwidth at ~1 micron.[169] An SWCNT film transferred to a silver mirror was also used to demonstrate sub-picosecond operational mode of optical fibre laser with the mode synchronization; Yb, Er and Tm : H doped fibres operating at 1, 1.56 and 2 microns, respectively were used. The scheme of the experimental setup with the fibre laser utilized in this study is shown in Fig. 16*a*. Parameters of the Yb doped fibre laser are presented in Fig. 16*b* as an example.

A method to prepare multifunctional free-standing SWCNT films, which allows one to adjust their thicknesses in the range from submonolayer to 200 nm, was reported.[170] These films can serve as high efficiency aerosol filters operating at low excess pressures, as electrodes with a sheet resistance of 84 Ω per square and transparency of 90%, as well as electrochemical sensors with low detection limit below 100 nmol $litre^{-1}$. In addition, these films were employed as major components of gas flowmeters, gas heaters, and transparent thermoacoustic loudspeakers. These films on supports can be utilized to create flexible

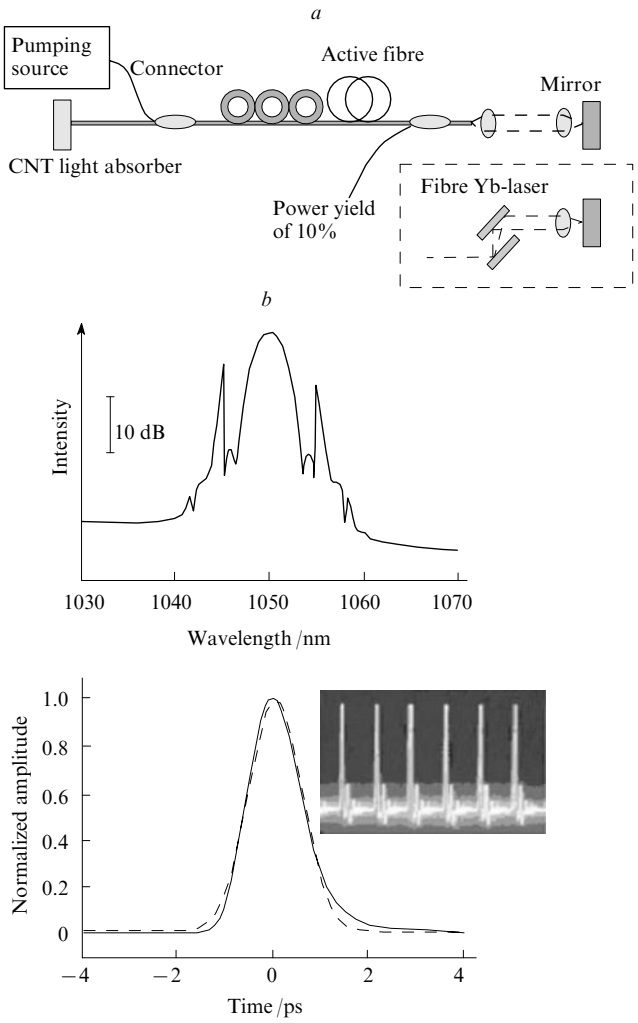


Figure 16. Diagram of the experimental setup with fibre laser (*a*) and characteristics of the fibre Yb-laser (*b*).[169]
(*b*) The insert shows oscillogram of the generated pulses.

electrodes for use in capacitive sensors and organic light-emitting diodes.[75]

Several methods are developed for twisting the nanotubes into the threads inside the reactor or at its outlet, they enable one to produce the threads of various configuration and treatment degree.[171] It was shown in the study of the effects from CNT length and structure on the mechanical properties of the threads that they display high elastic modulus and high rupture strength and significantly exceed analogous commercial fibres in these parameters. It was also demonstrated that these threads are more stable against mechanical tensions than Kevlar and can be used to fabricate light bulletproof jackets and other items with high ability to energy absorption.

* * *

The methods for the aerosol synthesis of SWCNTs have been shortly considered in this review. It has been shown that SWCNT growth conditions and processes can be studied by the methods known in the aerosol science. The capability to control the processes of growth and deposition of SWCNTs from the gas phase has been discussed.

One of the major advantages of the aerosol synthesis consists in production of SWCNTs suitable for further direct utilization in various applications without laborious purification, dispersion of the samples in liquids and subsequent deposition. The single-walled carbon nanotubes produced by the aerosol method contain almost no amorphous carbon or other undesirable impurities and the amount of the encapsulated metallic catalyst in them is low, therefore they can be used without subsequent treatment. The authors hope that in the nearest future this will be implemented in various products, which will appear in the market of microelectronics.

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