

CVD synthesis of multi-walled carbon nanotubes with integrated by-product recycling

N.I. Salmanova¹, A.B. Huseynov¹, E.B. Zeynalov^{1,*}, E.N. Aliyev¹, Z.E. Bayramova¹, A.Y. Guliyeva¹, E.B. Huseynova, K.V. Amirmatova², E.A. Ismailova¹, T.A. Isgandarova¹

¹Scientific Research Institute “Geotechnological Problems of Oil, Gas and Chemistry”, Ministry of Science and Education of Azerbaijan, Dilara Aliyeva Street 227, AZ1010 Baku, Azerbaijan.

²Azerbaijan State Oil and Industry University, "Nanomaterials and nanotechnologies" Scientific Research Laboratory

Abstract. The article is dedicated to the development of a large laboratory setup for CVD synthesis of multi-walled carbon nanotubes (MWCNTs), whose key feature is the targeted utilization of the resulting gaseous byproducts. Ferrocene was used as the catalyst precursor and acetonitrile served as the feedstock. The original design of the setup includes two consecutively connected reactors: the first carries out the CVD synthesis of MWCNTs, while the second is intended for utilizing the polycyclic aromatic hydrocarbons (PAHs) formed as byproducts during the process, using them as raw material for repeated thermal decomposition. The pyrolysis temperature for PAHs was set at around 1150 °C, which allows the conversion of harmful compounds into non-toxic carbon materials such as soot, coke and various carbon nanostructures.

Keywords: two-section laboratory setup for the synthesis of carbon nanotubes, CVD synthesis, carbon-containing feedstock, acetonitrile, ferrocene as a precursor-catalyst, multi-walled carbon nanotubes.

*Corresponding author.+994503512754

E-mail elzey@mail.ru (E.B. Zeynalov)

1.Introduction. Carbon nanotubes, like fullerene and graphene, are innovative basic carbon nanomaterials that form the foundation for the modern development of carbon nanotechnologies. Multi-walled carbon nanotubes (MWCNTs) can be used as effective nano-adsorbents, catalyst carriers, components of various types of composite materials, components for the manufacture of micro- and nanoelectronics parts, and in many other fields. The synthesis of carbon nanotubes and their extensive research worldwide began in 1991. In Azerbaijan the first synthesis of MWCNTs was carried out in 2012 at the Center for High Technologies under the Ministry of Communications and High Technologies of the Republic of Azerbaijan. The production of MWCNTs was achieved using a proprietary German installation (Fig. 1) [1-4].



Figure 1. Aerosol CVD installation for the synthesis of MWCNTs made in Germany.

The design of the costly installation was distinguished by its process automation for synthesis. The dimensions of the installation were: length 2 meters, width 70 cm, and height 2 meters. The installation consists of an ultrasonic raw material evaporation unit, a gas flow control unit (argon, hydrogen), a reactor unit, a temperature control unit, and a vacuum unit. The reactor unit comprises a horizontally arranged quartz tube with a diameter of 40 mm and a length of 1 meter, which is heated by a tubular muffle furnace moving at a set speed (1-100 mm/min) from one end of the reactor to the other. Work at the High Technology Center was carried out under the supervision of Professor Sevda Abdullayeva, with key specialists responsible for MWCNT synthesis being Doctor of Philosophy in Physics and Mathematics Nakhida Musaeva and Doctor of Philosophy in Chemistry Asgar Huseynov. Several scientific projects based on the synthesized MWCNTs were implemented, including within the framework of NATO grants, the first Azerbaijan-Russia grant, as well as the Republican SOCAR grant. Research on the development of carbon nanotechnologies at the High Technology Center continued until 2020. From 2020 onwards, MWCNT synthesis in Azerbaijan was continued at the Institute of Catalysis and Inorganic Chemistry named after academician M. Nagiev, in the laboratory of corresponding member Professor Eldar Zeynalov, using a large-scale laboratory CVD installation manufactured by Asgar Huseynov (Fig. 2) [5-12].



Figure 2. Universal laboratory CVD system for the synthesis of carbon nanotubes and carbon microtubes. 1 - gas preparation unit, 2 - reactor unit, 3 - furnace temperature unit, 4 - air supply unit, 5 - vacuum unit

The dimensions of the unit were: length 2 m, width 70 cm, height 1.90 m. Unlike the German unit the device produced was universal. Firstly, it was designed to use both gaseous and liquid raw materials, and secondly, the reactor block utilized a two-section furnace with independent temperature control in each section. In addition, the design and construction of the unit allowed syntheses to be carried out in the reactor with the furnace and reactor positioned either horizontally or vertically. Under the supervision of Professor Zeynalov the development of carbon nanotechnologies is being carried out in the following directions: the use of nano-carbon catalysts for aerobic and peroxide oxidation of petroleum hydrocarbons; utilization as modifying additives in cement-concrete composite materials; polymer material chemistry as fillers and stabilizing agents; and for the creation of electrically conductive polymer and ceramic materials.

It is known that during the synthesis of multiwalled carbon nanotubes (MWCNTs) by standard CVD methods toxic condensed polyaromatic compounds are produced as by-products, such as naphthalene, anthracene, phenanthrene, azulene, etc. Therefore, the obtained MWCNTs must be purified from these toxic products and the condensed polyaromatic compounds themselves should be disposed of—hence, such synthesis is associated with the risk of environmental pollution. That is why, in this study, the task was set to develop an environmentally friendly MWCNT synthesis method. In this regard, along with research on carbon nanotubes at the Institute of Catalysis and

Inorganic Chemistry by Professor Eldar Zeynalov and PhD Askar Guseynov, in cooperation with employees of the Research Institute "Geotechnological Problems of Oil, Gas, and Chemistry," in the laboratory "Catalysis and Oil Refining" led by PhD Nazilya Salmanova, a large pilot laboratory unit was designed, manufactured, and put into operation, intended for the environmentally friendly synthesis of MWCNTs. The scientific and technological novelty of this approach lies in the fact that during the synthesis of MWCNTs, the by-product toxic polycyclic aromatic hydrocarbons (PAHs) formed in the first reactor are fed into the second reactor and are disposed of by being converted into non-toxic carbon materials—soot, coke, as well as MWCNTs.

2. Experimental section

2.1 Experimental Apparatus. The manufactured and commissioned installation for environmentally friendly MWCNT synthesis is shown in Fig. 3.



Figure 3. CVD installation for environmentally friendly synthesis of multiwalled carbon nanotubes.

The dimensions of the setup are: length 2 m, width 1 m, height 2 m. As can be seen from the diagram, the setup consists of a temperature control block for two furnaces, a reactor block containing two muffle furnaces with quartz tube reactors, a liquid feed system, and a vacuum unit. Acetonitrile was used as the feedstock and ferrocene was used as the catalyst precursor. Before starting the experiment, the required amount (0.45 g, 0.9 g, 1.8 g) of ferrocene was dissolved in 50 ml of acetonitrile, and the resulting solution was added to the liquid feed system. After setting the temperature to 900°C, a gas mixture of hydrogen and argon was supplied to the reactor at flow rates of 12 L/h and 60 L/h, respectively. The liquid feed (with the dissolved catalyst precursor) was supplied at a rate of 1 ml/min. The synthesis duration was 50 minutes. The gas mixture (argon and hydrogen) and the liquid feed were directed into the first reactor at a temperature of 900°C, where the synthesis of MWCNTs occurred. To dispose of the side products (PAHs) formed in the first reactor, the gas stream was passed into a second reactor, where they were decomposed at a temperature of 1150°C.

2.2. Analysis of Reaction Products. The synthesized carbon nanotubes were identified by scanning electron microscopy (SEM) using a TESCAN VEGA3 microscope.

2.3. Reagents Used. Acetonitrile (99.5% pure), ferrocene (99.9% purity, Sigma Aldrich), hydrogen supplied by a hydrogen generator model ГВЧ-6, argon with 99.9% purity supplied from a gas cylinder manufactured in Russia.

3. Results and Discussion. For the selective growth of multiwalled carbon nanotubes (MWCNTs) this study investigated the use of ferrocene as a precursor-catalyst. Figure 4 shows the dependence of multiwalled carbon nanotube yield on ferrocene concentration.

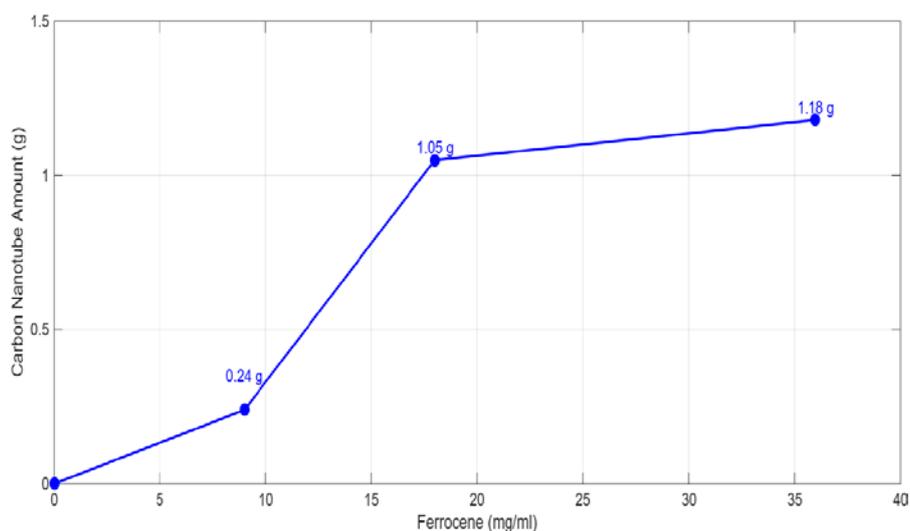


Figure 4. Dependence of multiwalled carbon nanotube yield on ferrocene concentration in the feedstock

From the graph, it can be seen that as the concentration of ferrocene in the feedstock increases, the yield of MWCNTs increases. However, the overall concentration of ferrocene cannot be increased beyond certain limits due to its solubility in acetonitrile. Depending on the amount of ferrocene, carbon nanotube deposits of varying amounts and diameters were obtained. Fig. 5 shows the SEM analysis of the carbon deposit synthesized at a ferrocene concentration in acetonitrile of 9 mg/ml.

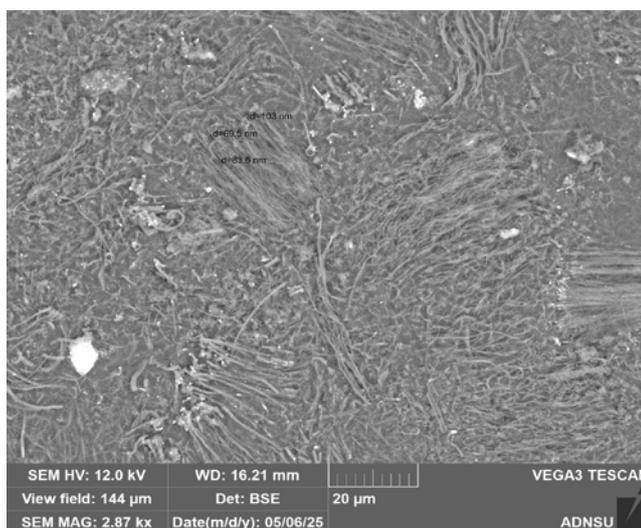


Figure 5. SEM analysis of multiwalled carbon nanotubes synthesized in the presence of ferrocene (9mg/ml)

The structures shown in Fig. 5 are fibrous and nanoscale. The fibers are densely intertwined and tangled. The image shows that the synthesized nanotubes are not isolated, but form agglomerates. As can be seen from Fig. 5, the diameters of the synthesized nanotubes are in the range of 80 to 100 nm.

Fig. 6 shows the SEM analysis of the carbon deposit synthesized at a ferrocene concentration of 18 mg/ml.



Figure 6. SEM analysis of multiwalled carbon nanotubes synthesized in the presence of ferrocene (18 mg/ml)

The synthesized material has a nanotubular structure and is of high quality and purity, as there are no other non-tubular carbon forms such as soot or coke visible in the image. As seen in Figure 6, the diameters of the synthesized nanotubes range from 100 nm to 200 nm.

Fig. 7 shows the SEM analysis of the carbon material synthesized at a ferrocene concentration in acetonitrile of 36 mg/ml.



Figure 7. SEM analysis of multiwalled carbon nanotubes synthesized in the presence of ferrocene (36 mg/ml)

The presented SEM image shows that the nanostructures have a tubular shape. The nanotubes are arranged parallel and densely packed, which indicates the maintenance of constant temperature and gas flow conditions during synthesis. It can be noted that no side non-tubular structures are observed in the image, indicating the high purity of the synthesized MWCNTs. As seen from Fig. 7, the diameters of the synthesized nanotubes are in the range of 100 to 300 nm. As can be seen from these images (Figs. 5–7), with an increase in the concentration of the catalyst precursor in the feedstock from 9 to 36 mg/ml, the diameter of the synthesized nanotubes increases from 80 - 100 nm to 100 - 300 nm. This effect - an increase in MWCNT diameter with increasing catalyst concentration

- can be explained based on literature data, according to which the diameters of synthesized MWCNTs are close to the diameters of the metallic catalyst clusters on which they form. We assume that as the concentration of the catalyst precursor increases, the cluster diameters also increase, leading to an increase in the diameter of the synthesized MWCNTs.

4. Conclusions. A large laboratory setup for environmentally friendly MWCNT synthesis has been developed, constructed, and put into operation. A two-reactor technology for the environmentally friendly synthesis of MWCNTs is proposed: in the first reactor carbon nanotubes are synthesized, and the toxic byproducts formed during synthesis are neutralized in the second reactor by high-temperature pyrolysis to yield non-toxic substances such as soot, coke, and nanotubes. Optimal conditions have been established for converting liquid acetonitrile feedstock, using ferrocene as the catalyst precursor, into high - quality and pure multiwalled carbon nanotubes. It has been shown that as the concentration of ferrocene in acetonitrile - in other words, as the catalyst - precursor - feedstock ratio increases the diameter of the synthesized nanotubes also increases.

Conflict of interest.

The authors declare that they have no conflict of interest in relation to this research.

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