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Growth of Carbon Nanowires and Nanotubes via Ultrarapid Heating of Ethanol Vapor

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Abstract—A method is proposed for producing carbon nanomaterials by ultrarapid heating of vapors of organic compounds to high temperatures, and an experimental setup for implementing this method is described. The starting reagents used are ethanol and mixtures of ethanol with water, glycerol, and ferrocene. At heater temperatures of 1500–2000°C and substrate temperatures of 600–1000°C, carbon nanowires and nanotubes are obtained. The nanowires attain 100 μm in length and range in thickness from 30 to 150 nm. The nanotubes have "bamboo" or "fish-bone" structures, with a thickness from 20 to 50 nm. The deposition of nanotubes on supported catalysts (iron, nickel, gold, and others) is also examined. It is shown that, under certain conditions, selective deposition of carbon nanotubes (nanowires) onto catalyst-coated parts of the substrate is possible.

INTRODUCTION

After the discovery of carbon nanotubes in 1991, considerable effort has been concentrated on the development of new approaches to producing nanotubes and optimization of the known methods. One of the most common and effective methods for producing nanotubes is arc vaporization [1]. The main drawback to this method is the formation of various carbon structures and carbonized catalyst particles, with a content of nanotubes no higher than a few tens percent. The separation of nanotubes from such mixtures and their purification requires much effort and time. Moreover, this method is unsuitable for growing uniform layers of carbon nanotubes on substrate surfaces.

In recent years, many studies have been devoted to nanotube growth via high-temperature (as a rule, catalyzed) decomposition of carbon compounds—acetylene [2], methane [3], carbon monoxide [3, 4], and others [5]. Typical catalysts are transition metals (often, iron-group metals) and their compounds [2–6]. However, classical pyrolysis with the use of a flow reactor and external heater (furnace) is of limited application because the process cannot be run continuously, the dimensions of the substrate are limited by those of the reactor, and the deposition temperature is, as a rule, no higher than 1000–1100°C. Moreover, since the reactor is heated throughout its length, the reaction mixture cannot be heated or cooled rapidly. At the same time, the factors in question are known to be of key importance in the formation of carbon nanomaterials [7]. Here, we describe a pyrolytic method which allows the above limitations to be overcome. The purpose of this work is to examine the potentialities of the proposed method with application to the pyrolysis of ethanol vapor and ethanol-based mixtures.

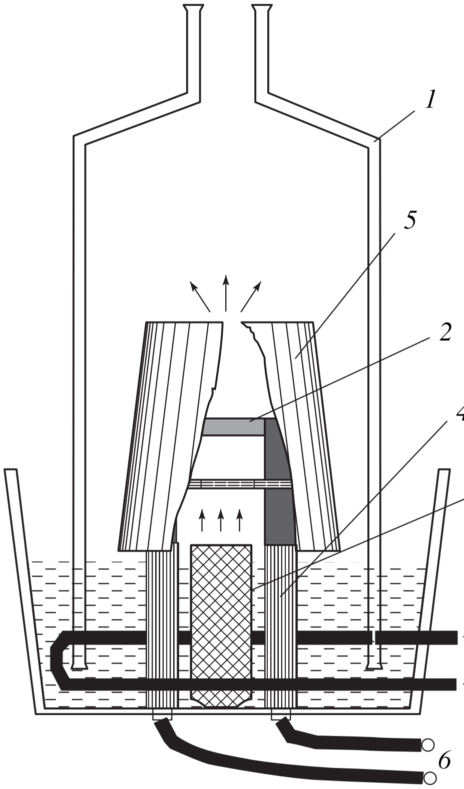

Fig. 1. Experimental setup for the preparation of carbon nanomaterials: (*1*) quartz reactor, (*2*) graphite heater, (*3*) source of the starting reagent, (*4*) current leads, (*5*) glassy carbon bell jar, (*6*) current source.

EXPERIMENTAL

The experimental setup is schematized in Fig. 1. The reaction mixture is heated by a graphite rod 50 mm in length and 5 mm in diameter, which is introduced into the reactor. This allows the thermal-activation zone to be separated from the deposition zone and the process temperature to be raised substantially (as compared to conventional pyrolytic methods), without raising the substrate temperature, which may even be reduced. Thus, pyrolysis occurs in a high-temperature zone near the heater. The reaction products either condense on the substrate, situated near the heater, or leave the reaction zone, together with the gas evolved. Another distinguishing feature of the method is ultrarapid heating of the reagent vapor, which is ensured by minimizing the separation between the cooled source of the starting reagent and the heater.

The heater temperature was varied from 1000 to 2000°C. As the starting reagent, we used ethanol and mixtures of ethanol with water, glycerol, and ferrocene. The reaction products were characterized by differential thermal analysis (DTA), x-ray diffraction (XRD), and scanning and transmission electron microscopy. In DTA, we used an RIF-5 precision temperature controller. The heating rate was 2°C/min. Analyses were carried out in flowing air (50 ml/min), which was delivered through a thin tube. The morphology of the deposits was examined on a JEOL JSM-840A scanning electron microscope (SEM). Their structure was analyzed on a JEOL JEM-2000FX transmission electron microscope (TEM).

Carbon nanomaterials were produced with or without catalysts. Some of the reaction mixtures studied contained ferrocene as a catalytic additive. As supported catalysts, we used iron, nickel, cobalt, gold, or $Fe_{0.7}Cr_{0.2}Ni_{0.1}$ films 100–200 Å in thickness. The films

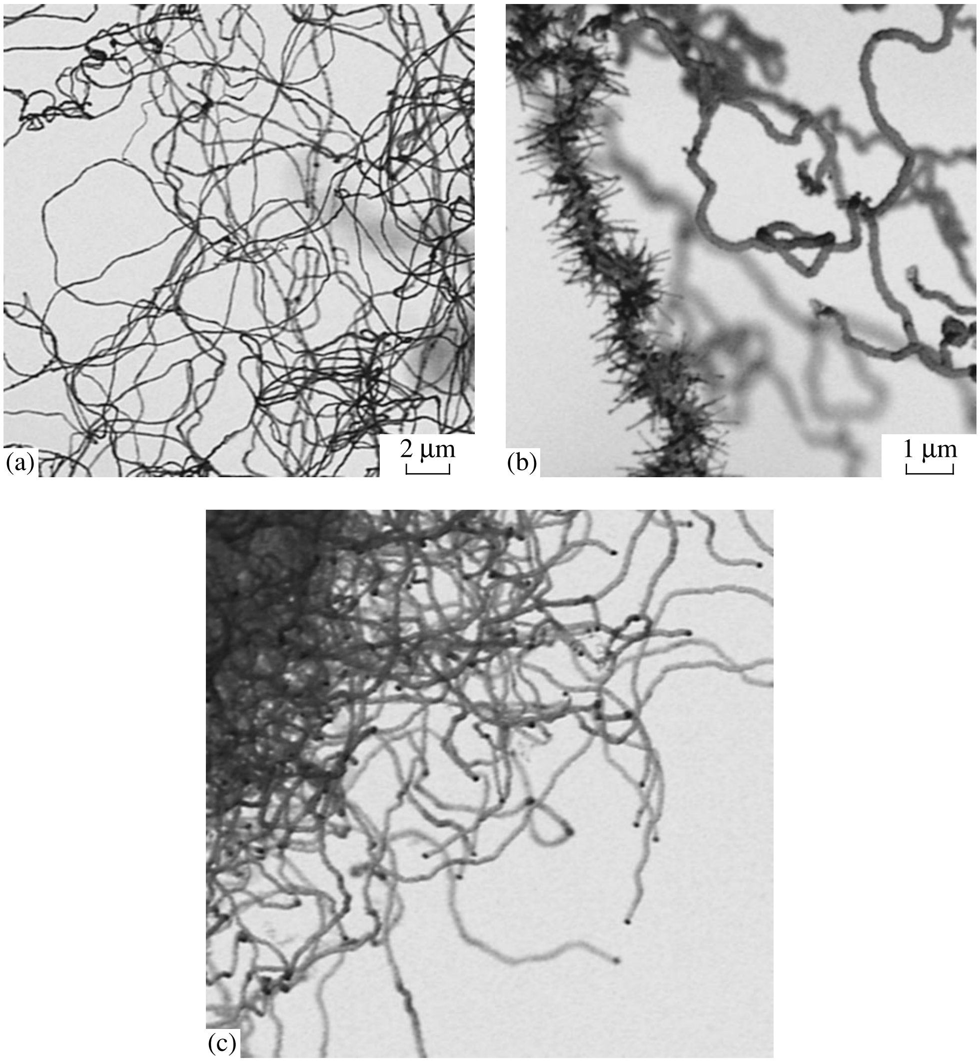

Fig. 2. SEM images of carbon nanomaterials produced by ultrarapid heating of ethanol vapor.

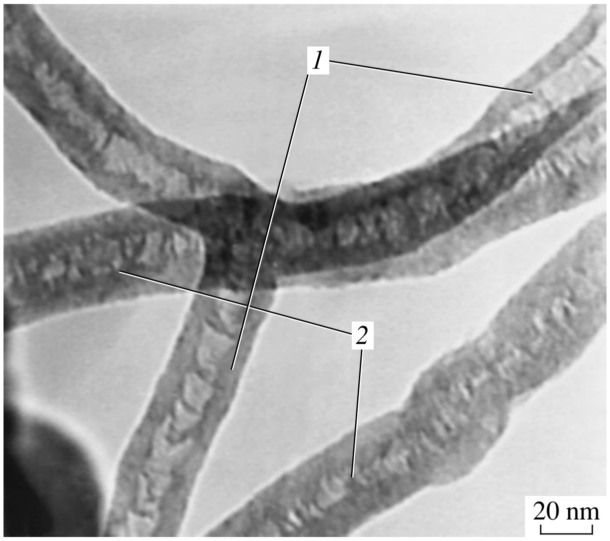

Fig. 3. TEM image of carbon nanotubes with (*1*) bamboo and (*2*) fish-bone structures produced by ultrarapid heating of ethanol vapor.

were deposited by thermal evaporation in a VUP-5 vacuum unit. Some of the samples were oxidized in air at 550°C for 5 h. The substrates were made of graphite or silicon.

RESULTS AND DISCUSSION

High-temperature reactions typically yield a mixture of different carbon structures. The composition of such mixtures can be determined by DTA because the oxidation temperature in oxygen depends on the carbon structure [8, 9]. Since the process is accompanied by heat release, the oxidation temperature is easy to determine by DTA and can be used to identify the carbon structure.

To ensure proper interpretation of DTA results, we first analyzed fullerene samples, graphite powder, fine-particle diamond powder, their mixtures, and noncrystalline carbon (activated carbon and fine-particle glassy carbon). Under the conditions of this study, the oxidation temperature (maximum peak temperature) was 520–530°C for fullerene, 730–760°C for graphite, and 920–930°C for diamond. Noncrystalline carbon was found to oxidize in the range 400–600°C.

Analysis of the bulk products obtained from ethanol vapor and a 1 : 1 mixture of water and ethanol at heater temperatures above 1200°C indicates the presence of noncrystalline carbon and a phase close in oxidation temperature to graphite. The DTA curves of the material deposited on a graphite substrate near the heater show only one peak corresponding to an oxidation temperature of 740–770°C. XRD examination reveals the

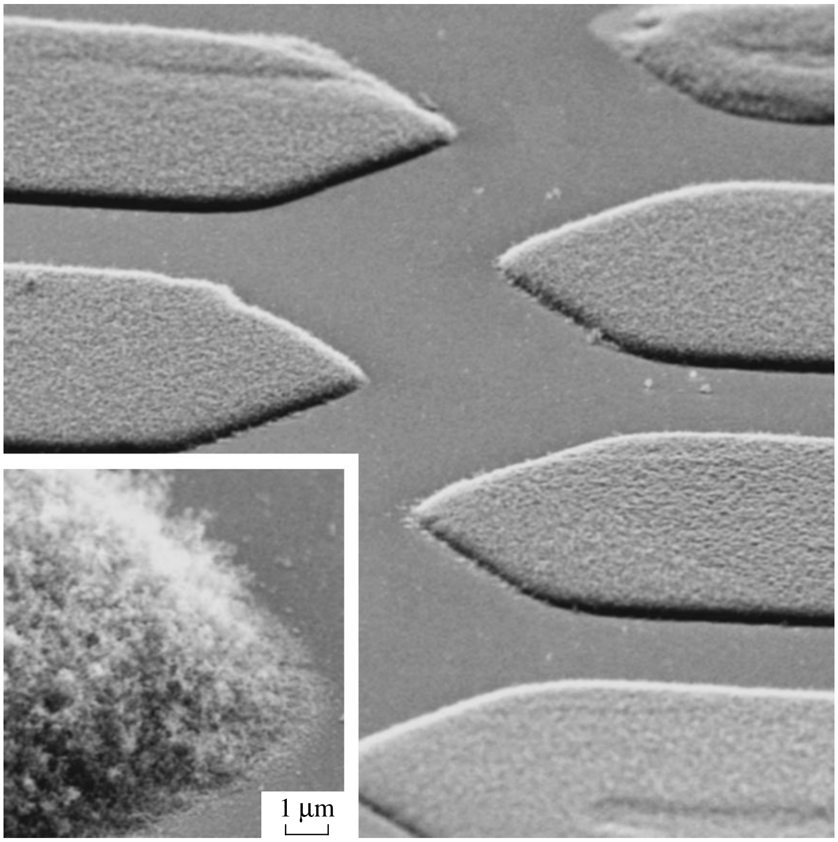

Fig. 4. Selective deposition of carbon nanotubes on a silicon substrate; the process was catalyzed by a 100-Å-thick $Fe_{0.7}Cr_{0.2}Ni_{0.1}$ film preoxidized in air at 550°C.

presence of graphene planes. Therefore, it seems likely that the deposit consists of multiwalled carbon nanotubes and nanowires, the closest analogues of graphite.

SEM examination demonstrates that the deposits on graphite substrates do have a fibrous structure (Fig. 2a). The nanowire length may attain several tens of microns, depending on the process duration. The growth rate of nanowires is 1–3 μm/min. Occasionally, we observe secondary nanowire growth, leading to the formation of garlandlike structures (Fig. 2b). The introduction of ferrocene vapor into the reaction mixture notably changes the deposit structure: the fibrous material becomes denser, and some nanowires are terminated with nanoparticles consisting of a material different from the deposit material (judging from the electron-microscopic contrast). The nanoparticles are close in diameter to the nanowires and seem to consist of iron metal or iron carbide (Fig. 2c).

The structure of the nanomaterials was studied in greater detail by TEM. The samples were found to consist of both nanowires and nanotubes. The nanowire thickness ranges from 30 to 150 nm. The nanotubes have "bamboo" or "fish-bone" structures (Fig. 3) with an outer diameter of 20–50 nm. Note that, according to electron-microscopic results, the samples contained insignificant amounts of nonfibrous material.

We also examined the potential of the proposed method for depositing a layer of nanotubes on supported catalysts. The process was found to be catalyzed by thin films of iron, nickel, cobalt, and their alloys. The catalytic effect was far more pronounced if the catalyst film was thermally oxidized in air. Gold was found to exhibit the highest catalytic activity. This finding is of considerable interest because the catalytic properties of the iron-group metals are well known, whereas little or no data have been reported on the catalytic activity of gold in the growth of carbon nanomaterials. Copper and aluminum films showed very low or no catalytic activity.

The catalytic effect of metals is well illustrated by the selective deposition of nanotubes on a silicon substrate coated with a patterned metal film: no nanostructures are formed on the uncoated parts of the substrate. An example of such a structure is shown in Fig. 4. The inset displays the fibrous structure of the deposit at an increased magnification.

The present results provide convincing evidence that the proposed method has great potential for producing carbon nanomaterials. Further, more in-depth studies are planned to assess the effects of the temperature, reaction medium, catalyst, and other factors on the effectiveness of the process and the phase composition and structure of the deposit.

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REFERENCES

1. Zhang, Y., Iijima, S., Shi, Z., *et al.*, Mass-Production of Single-Wall Carbon Nanotubes by Arc Discharge Method, *Carbon*, 1999, vol. 37, no. 9, pp. 1449–1453.
2. Mo, Y.H., Kibria, A.K.M.F., and Nahm, K.S., The Growth Mechanism of Carbon Nanotubes from Thermal Cracking of Acetylene over Nickel Catalyst Supported on Alumina, *Synth. Met.*, 2001, vol. 122, no. 2, pp. 443–447.
3. Chen, P., Zhang, H.-B., Lin, G.-D., *et al.*, Growth of Carbon Nanotubes by Catalytic Decomposition of CH_4 or CO on a Ni–MgO Catalyst, *Carbon*, 1997, vol. 35, no. 10/11, pp. 1495–1501.
4. Thaib, A., Martin, G.A., Pinheiro, P., *et al.*, Formation of Carbon Nanotubes from the Carbon Monoxide Disproportionation Reaction over Co/Al_2O_3 and Co/SiO_2 Catalyst, *Catal. Lett.*, 1999, vol. 63, no. 3/4, pp. 135–141.
5. Bento, A.M., Maniette, Y., Munoz, E., and Martinez, M.T., Carbon Nanotubes Production by Catalytic Pyrolysis of Benzene, *Carbon*, 1998, vol. 36, no. 5/6, pp. 681–683.
6. Hernadi, K., Fonseca, A., Nagy, J.B., *et al.*, Fe-Catalyzed Carbon Nanotube Formation, *Carbon*, 1996, vol. 34, no. 10, pp. 1249–1257.
7. Rakov, E.G., Methods of Carbon Nanotube Production, *Usp. Khim.*, 2000, vol. 69, no. 1, pp. 41–59.
8. Alvarez, W.E., Kitiyanan, B., Borgna, A., and Resasco, D.E., Synergism of Co and Mo in the Catalytic Production of Single-Wall Carbon Nanotubes by Decomposition of CO, *Carbon*, 2001, vol. 39, no. 5. pp. 547–558.
9. Park, Y.S., Choi, Y.C., Kim, K.S., *et al.*, High Yield Purification of Multiwalled Carbon Nanotubes by Selective Oxidation during Thermal Annealing, *Carbon*, 2001, vol. 39, no. 5, pp. 655–661.