Synthesis of carbon nanotubes on catalysts prepared by solution combustion on glass-fibers

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Abstract

In this paper we present results of the synthesis of carbon nanotubes on glass-fibers (GF) catalysts. For the synthesis of carbon nanotubes we used compounds of transition metals, such as Fe and Co. The synthesis of the catalyst was carried out by solution combustion synthesis on GF. The content of the active component is 2 – 5%. Synthesis of carbon nanotubes was carried in the CVD-system. For the catalyst of GF – Co_3O_4 (5%) type carbon nanotubes are formed with diameters from 25 nm up to 35 nm, which are all intertwined, forming a three-dimensional disordered structure. For GF - Fe_2O_3 (2%) type catalyst a complex of carbon nanotubes with carbon nanofibers are formed with diameters in the range of 9 - 25 nm. Significant number of nanotubes has a spiral structure with 14 - 15 nm diameters.

Introduction

Carbon nanotubes have unique physical and chemical properties and have been named «material of the future» [1,2]. Due to their properties, carbon nanotubes (CNT) are used in various fields such as energy, biotechnology, microelectronics, et. al. [3,4].

The structure and properties of carbon nanotubes depend on many factors: the initial components in synthesis, the composition and morphology of the catalyst, synthesis conditions, etc. [5]. Not infrequently for the synthesis carbon nanotubes, the catalyst is a system consisting from the active phase and the matrix. As the matrixes for the catalyst silicon wafers [5], mesoporous silica [6], zeolites [7], aerogels, quartz, sapphire [8] and others are used. Selection of the matrix for the active phase of the catalyst and particularly its structure largely determines the properties of the final CNT product. Creation of new catalytic systems with various combinations of active phase and matrix, allows tosynthesize carbon nanotubes with various morphology and properties. In [9], the authors report the synthesis of carbon nanotubes and nanofibers on fiberglass with palladium catalyst (1 and 2% mass.). However, in [9] the samples need 3 hour treatment in N_2/H_2 at 400°C, and growth time of carbon nanomaterials is about 2 hours. The use of glass fiber fabrics is justified by their high levels of chemical stability and mechanical properties: resistance to high temperatures, chemical resistance, flexibility and the ability to create various geometric forms.

Nanosized catalytic systems can be effectively used for the solution of ecological problems of processes of CO and hydrocarbon combustion as well as for the utilization of components, which cause the so-called “greenhouse effect” [10, 11]. Main components of a greenhouse gas are water vapor, CO_2, CH_4 and O_3 [12]. The utilization of CO_2 and CH_4 is of great interest because these substances can be used as reactants for the dry reforming of methane to yield hydrogen or synthesis of natural gas [13-15], which are a valuable feedstock for the production of ultraclean fuels [16].

Lately quite sizable data on the use of catalysts based on glass fiber in many other chemical processes have appeared[17-20]. It is shown that catalysts on the basis of glass fiber are highly active even at a low content of the active catalytic component on the surface of the support.

This work is devoted to the development of nanosized catalysts via formation of low-percentage Co_3O_4, Fe_2O_3 active components on glass fiber support by a “solution combustion” (SC) method. The chosen method of preparation allows uniform heating of the catalyst at low temperature (400°C) initiating the combustion front on the surface of catalyst, and the low content of active components will limit the development of a high temperature wave by preventing the overheating of the catalyst.

Experimental part

Synthesis of catalysts

For the synthesis of carbon nanotubes compounds of transition metals: Fe, Co have been used. When selecting the catalysts it is necessary to consider the nature of the transition metal. In a number of transition metals of Ti to Ni, when filling of *d* – level by electrons decrease strength in the bond of M-C of these metals. The formation of strong chemical bonds between metals Ti, V, Cr and carbon causes their low catalytic efficiency. In this work oxides of cobalt and iron were used as the catalysts.

A silica glass fiber (SGF) used in experiments consists of filaments with diameter of 6-7 μm. After removing of a lubricant, the glass fiber was leached in a 5.5% solution of nitric acid for 1 h at 90°C, washed with water to obtain pH = 5.5-7, dried and calcinated at 300°C in air. The properties of SGF after the pretreatment are as follows: S_{BET}^{Ar} is 1 m^2/g,V_{pore} is 0.0006 cm^3/g, amorphous phase is proved by XRD.

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Ni and Fe oxides were deposited onto the surface of a glass fibers matrix by the method of "solution combustion", which is one of the versions of a self-propagating high temperature synthesis [21].

Glass fibers of a definite size were impregnated with a solution of cobalt and nickel nitrates, after that they were dried for 30 minutes in air at 100°C and then calcinated in air atmosphere at 400°C. At this temperature the self-propagating high temperature synthesis resulted in the formation of nanoparticles with the size from 30 to 100 nm [22-24]. The SC method between initial components (Co nitrates and Fe chlorate + glycine) corresponds to the following reaction.

$$3Co(NO_3)_2 \cdot 6H_2O + 6C_2H_5NO_2 + 0.5O_2 = 12CO + 33H_2O + 6N_2 + Co_3O_4$$

(cobalt nitrate)

$$3FeCl_3 \cdot 6H_2O + C_2H_5NO_2 + 3.5O_2 = 2CO + 20.5H_2O + 0.5N_2 + 4.5Cl_2 + 1.5Fe_2O_3$$

(ferric chloride)

$C_2H_5NO_2$– glycine acts as the reducing agent.As a result of the reaction, the formation of nanoparticles with sizes ranging from 10 to 50 nm was achieved [23].

Physicochemical examination of samples

The specific surface area (S_{BET}, m^2/g) of samples was determined by the method of thermal desorption of argon (BET method) on a device SORBI N.4.1 by comparing volumes of gas – adsorbate (argon), being sorbed by the sample under the study and the standard sample of the material with the known specific surface area.

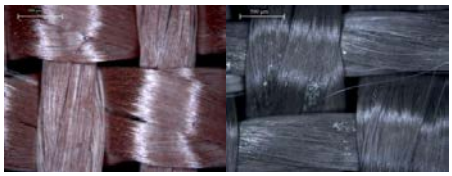
X-ray diffraction (XRD) patterns were recorded using a HZG-4Cdiffractometer with CoKα (λ=1.79021Å) radiation. Sample patterns were taken by a point scanning with 0.05 degrees with accumulation of 18 s at each point in the range of angles 20-80°. To make the certain phase composition and to determine parameters of the lattice, we additionally carried out the point scanning with the step of 0.05° with the accumulation of 36 -60 s at each point in the range of angles 70-80°. The average size of crystallites was estimated in accordance with the Sherrer equation. An analysis of the crystalline structure of samples was carried out using the JCPDS Database.

The SEM study was performed using Zeiss-LEO Model 1530 Variable Pressure Field Effect SEM microscope with accelerating voltage 25 kV. For local analysis of chemical composition of a sample, the microscope is equipped with an EDAX energy dispersive X-ray spectrometer (INCA OXFORD Instrument).

Results and Discussion

Characteristics and properties of the catalysts

Figure 1 shows optical microscope photographs catalysts on glass fiber fabrics with Co_3O_4 and Fe_2O_3 (3 wt. %).



Fe_2O_3 Co_3O_4

Figure 1 – Optical microscope photographs catalysts on glass fiber fabrics with Co_3O_4 and Fe_2O_3 (3 wt. %).

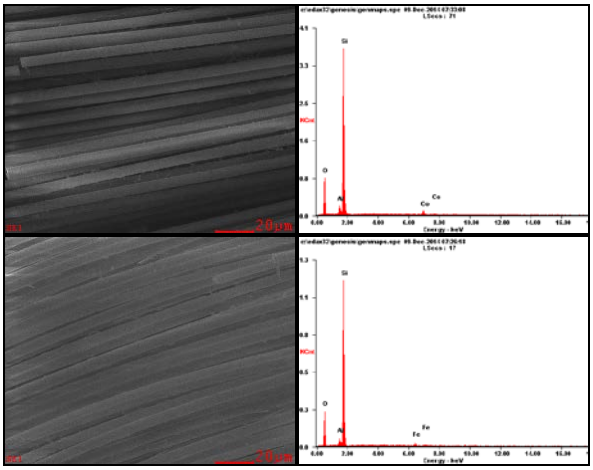


Figure 2 – EDX spectra of glass fiber fabrics catalysts with Co_3O_4 and Fe_2O_3 (3 wt. %)

To establish a structure derived metal oxides was carried out X-ray analysis of the samples. Figure 3 shows the diffractogram for the glass fabric with Co_3O_4 and Fe_2O_3 (3 wt. %).

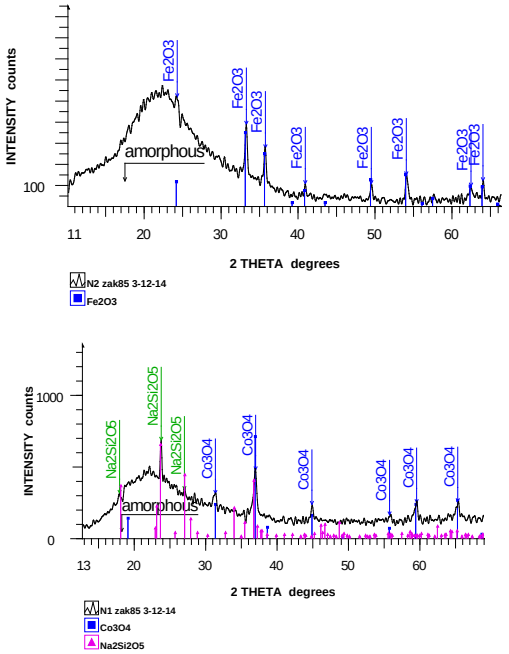


Figure 3 – X – ray diffractograms for the glass fabric with Co_3O_4 and Fe_2O_3 (3 wt. %)

Table 1. Characteristics of catalysts on glass fiber fabrics

Catalyst	Salt used for impregnation	Reducing agent	The active ingredient content, wt. %
Glass fiber fabrics – Co_3O_4	$Co(NO_3)_2 \cdot 6H_2O$	Glycine	5 %
Glass fiber fabrics – Fe_2O_3	$FeCl_3 \cdot 6H_2O$	Glycine	2 %

Synthesis of carbon nanotubes on the glass fiber fabrics by chemical vapor deposition

Synthesis of carbon nanotubes carried on the installation for chemical vapor deposition, consisting of an oven with three heating zones, a quartz tubular reactor. Gas flow: He - 650 cm^3/min, H_2 - 150 cm^3/min, C_2H_2 – 19.5 cm^3/min. Temperature - 710 °C, time of synthesis - 20 min.

Results and discussion

The resulting carbon nanotubes were examined using a scanning electron microscope (Zeiss-LEO Model 1530 Variable Pressure Field Effect Scanning Electron Microscope). Figure 4 shows SEM photographs of carbon nanotubes grown on glass fiber fabrics with Co_3O_4 (5 wt.%).

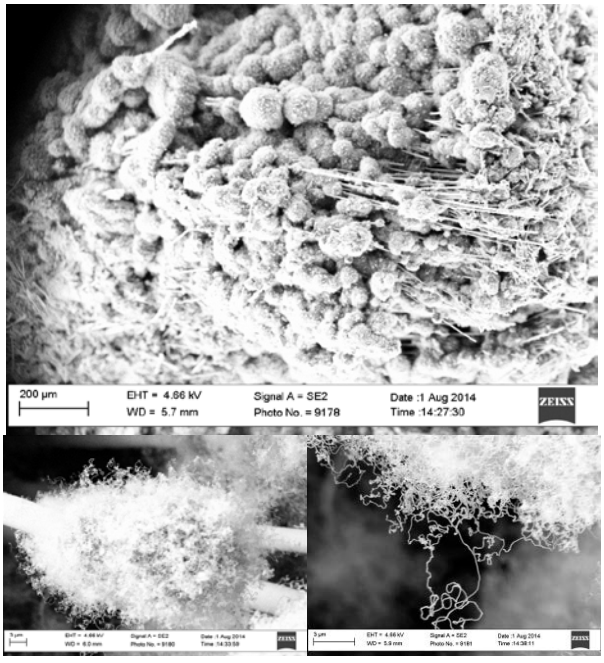


Figure 4 – SEM photograph of carbon nanotubes grown on glass fiber fabrics with Co_3O_4 (5 wt.%)

Figure 5 shows TEM images of carbon nanotubes grown on glass fiber fabrics with Co_3O_4 (5 wt.%) catalyst.

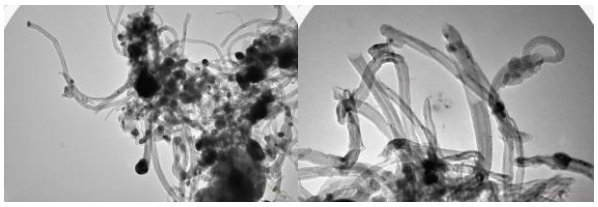


Figure 5 – TEM image of carbon nanotubes grown on glass fiber fabrics with Co_3O_4 (5 wt.%)

As can be seen from the TEM images carbon nanotubes have diameters of 25 – 35 nm, and are all intertwined, forming a three-dimensional disordered structure.

Figure 6 shows an SEM pictures of carbon nanotubes grown on glass fiber fabrics with Fe_2O_3 (2 wt.%) catalyst.

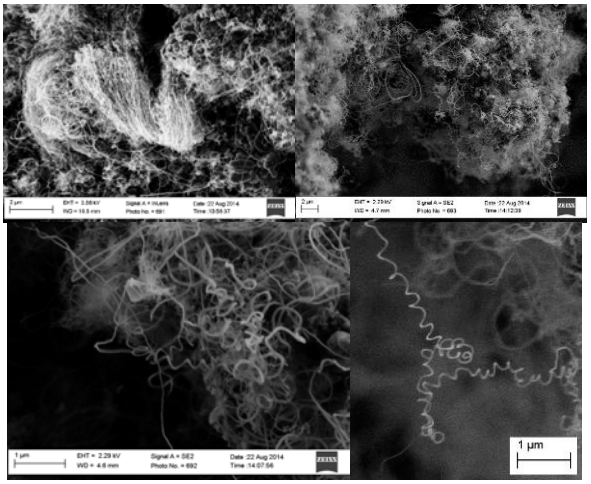


Figure 6 – SEM pictures of spiral carbon nanotubes grown on glass fiber fabrics with Fe_2O_3 (2 wt.%) catalyst

Figure 7 shows TEM images of carbon nanotubes synthesized on the fiberglass with Fe_2O_3 (2 wt.%) catalyst.

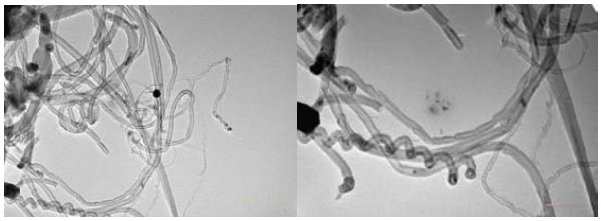


Figure 7 – TEM image of carbon nanotubes grown on glass fiber fabrics with Fe_2O_3 (2 wt.%)

As seen from the TEM images, samples of carbon nanotubes with diameters ranging from 9 to 25 nm. were obtained in the synthesis Also, the sample contained a small amount of amorphous carbon phase. Spiral nanotubes have diameter is 14 – 15 nm.

Investigation of the current-voltage characteristics of carbon nanotubes on the glass fiber fabrics

Current-voltage characteristics of fiberglass with CNTs obtained by CVD were measured. Pure fiberglass is dielectric. To remove the amorphous carbon phase, sample was treated by 38% solution of hydrogen peroxide for 24 hours. Residual hydrogen peroxide was removed by distilled water. The area of the sample was 4.95 cm^2. This sample has a resistance R = 1.8 Ω and sheet resistance of R_{sp} = 0.3636 Ω/cm^2.

Figure 8 – Measurement of the resistance of fiberglass with CNT

Figure 9 shows the current-voltage characteristics for fiberglass with CNTs.

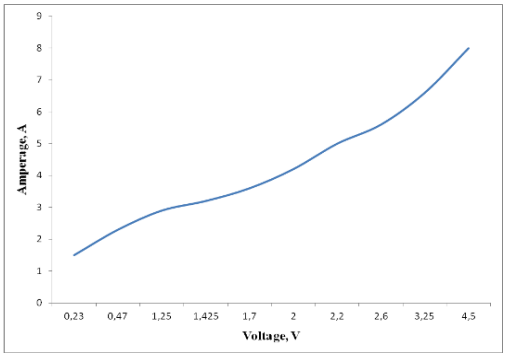


Figure 9 – Current-voltage characteristics of the sample fiberglass – CNT

Figure 10 shows the dependence of the temperature of the sample glass with CNT on the power.

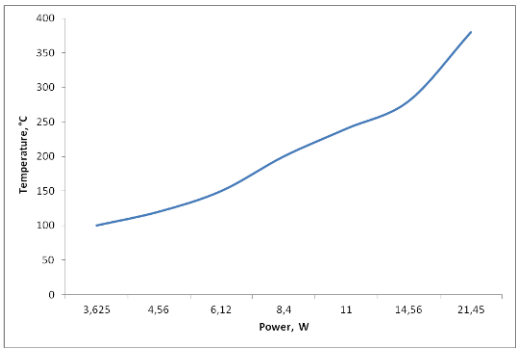


Figure 10 – Changing the sample temperature fiberglass – CNT at different values of the power

So when the amperage of 1.25 A, the sample was heated to a temperature of 100 °C. With a value of 3.25 A temperature was 380 °C.

As can be seen from the above data CNT are good conductors of electrical current, which gives an effective Joule heating. Such fabrics can be used for solar water heaters with external heating. Similar work conducted in NanoTechInstiute [25]. The use of composite of a glass cloth – CNT has a number of advantages. If there is no sunlight is possible to heat the water by feeding the small current (10 – 20 V).

Measurement of current-voltage characteristics of the array of carbon nanotubes grown on glass cloth.

In this experiment, under the "array" of carbon nanotubes, carbon nanotubes are taken randomly oriented in space and do not have an ordered structure.

Weight of carbon nanotubes synthesized on the glass cloth with cobalt oxide was ~ 0.34 g. Carbon nanotubes were placed in a quartz capillary of 5 cm length and an inner diameter of 1 mm. As contacts gold-plated wire was used with a length of 1 cm. The resistance of this sample was 27.8 Ω. Current-voltage characteristics for the sample at various temperatures from 25 to 350 °C were investigated (Fig. 11).

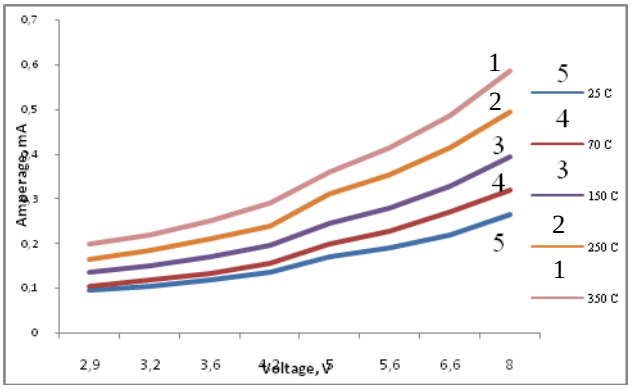


Figure 11 – Current-voltage characteristics of the array of carbon nanotubes at different temperatures

Conclusions

Co and Fe nano-catalysts prepared by combustion on glass fiber textile substrates allows to grow various types of CNT and carbon fibers standard by CVD method. The CNT on GF textiles have quite interesting electrical properties, as proved by I-V curves strongly depending on the temperature. This type of conductive CNT@fiberglass textiles can be used for various functional applications, such as selective black coatings for solar water heaters. Such CNT @ GF coatings have an advantages of Joule heating by externally applied current in the absence of sun.

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