INVESTIGATION OF INFLUENCE OF INITIAL COMPONENTS ON SYNTHESIS OF COBALT OXIDES BY SOLUTION COMBUSTION SYNTHESIS

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Abstract

For the synthesis of cobalt oxide nanoparticles, the method of solution combustion was used. As initial components cobalt nitrate and glycine was used. The influence of the ratio of the initial components on the particle size was investigated. It was found that adding of nitric acid leads to the formation of more dispersed nanoparticles. In the case adding nitric acid formed nanoparticles with a small distribution of from 4 to 16 nm. For particles of cobalt oxide at a ratio φ = 1.5 particle size ranges from 20 to 65 nm, without big agglomerates. Cobalt oxides nanoparticles was deposited onto glass cloth for synthesis of carbon nanotubes.

Introduction

Cobalt oxide is often used in the glass industry. It is a stable and intense colorant (pigment) for glass products. The color of the cobalt compounds is very constant and does not depend on the cooking regime. When using cobalt compounds in combination with other dyes, glasses with different shades can be obtained. In the chemical industry, it is used as a catalyst for various chemical processes. It is also used in the electrical industry for the production of capacitors, and negative battery electrodes. There are various methods for synthesis of Co_3O_4 nanoparticles, such as: chemical synthesis using of precipitation method [1], hydrothermal synthesis [2], template method [3]

In [4] nanoparticles of Co_3O_4 was obtained by combustion synthesis using nitrates-aspartic routes each with different fuel ratio (ranging 0.5-2.5). Authors found that obtained Co_3O_4 nanoparticles have size ranging between 21 and 76 nm.

Method of solution combustion are using for obtaining of CoO/graphene/Co_3O_4 nanoparticels composites [5]. This composite as electrodes of lithium ion battery was used. The Co_3O_4/CoO/graphene nanocomposite electrode delivered an initial charge capacity of 890.44 mAh/g and Exhibit 90 % of good capacity retention 801.31 mAh/g after 30 cycles.

The solution com method helps to obtain the catalyst in powder form - during the process in aqueous medium, or to synthesize the nanoparticles directly at the surface of specified material (the matrix) - by impregnation or wetting the matrix material with solutions of primary components. The principle of method consists in reaction behavior with the formation of metal oxide as final product, also the metal salts such as (mostly nitrates, chlorides or acetates) used as initial reagents, they mixed with organic compounds (glycine, citric acid, urea, ascorbic acid, etc.), the mixing is carried out at the molecular level, by solution preparation of primary components.

Experimental part

The basis of the synthesis of ultrafine metal oxide particles contains an exothermic process of liquid-phase interaction system components, including fuel and oxidation agent. General formula that describing the exothermic chemical reaction using metal nitrate as oxidant, glycine as fuel, can be represented as follows:

$$M^{v}(NO_3)_v + (5/9v\varphi)CH_2NH_2COOH + 5/4vF(\varphi)O_2 \rightarrow M^{v}O_{v/2}\downarrow + (10/9v\Phi)CO_2\uparrow + 25/18\varphi H_2O\uparrow + v(5\varphi + 9/18)N_2\uparrow$$

where M – is the metal;

ν – is the valent of metal;

φ – is the ratio of fuel and oxidant.

$F(\varphi)=(\varphi-1)$ at $\varphi \geq 1$ and $F(\varphi)=0$ at $\varphi<1$. In case $\varphi>1$ for oxidation it is required the atmospheric oxygen; $\varphi = 1$ the atmospheric oxygen is not necessary.

Nitrates of related metals were used as starting reagents. For obtaining of cobalt oxide - cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), glycine ($C_2H_5NO_2$) as fuel and nitric acid were used (glycine-nitrate synthesis). As the oxidizing agent in this case act nitrate-ions present in the solution. The reagents were completely dissolved in distilled water in a heat-resistant glass, and then evaporated to a volume of 5 - 7 ml. After evaporation, the reaction mixture was heated to 260 °C after which autoignition of solution was observed. Auto-ignition temperature has been selected on the basis of the decomposition temperature of glycine, where the decomposition of glycine with increased temperature up to 1200 °C is occurred. At this temperature, an instantaneous ignition of the mixture is occurred and the final product is deposited directly on the walls of glass. The reaction product is an ultrafine black powder. A schematic illustration of the process of obtaining cobalt oxide nanoparticles by solution combustion method is shown in figure 1 [6].

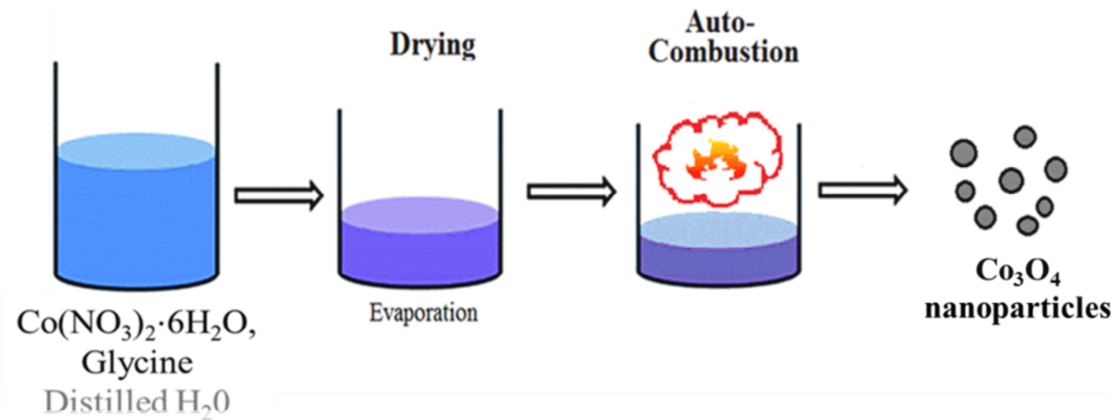


Figure 1 – Scheme of obtaining cobalt oxide nanoparticles by solution combustion method [6]

To determine the ratio influence of oxidant and fuel on dispersion of final product some studies were conducted at various oxidant-fuel ratio – 1:1; 1:1,5 with adding nitric acid.

This method to deposit of Co_3O_4 nanoparticles onto glass cloth was used. The fiberglass (brand ST-11) was used as a basis for deposition. This type of glass cloth comprises 98-99 % of SiO_2, surface density is 300 g/m^2, thickness is 0,35-0,4 mm and it is resistant to continuous exploitation at a temperature of 1000 - 1200 °C without changing of its structure; the volume reduction at heat treatment does not exceed 3 wt. %, it is resistant to strong acids and alkalies, and environmentally safe.

The concentration of active component at the surface of fiberglass was 3 % by weight. For preparation of catalysts, the fiberglass sample with the size of 5 cm^2 was washed with ethyl alcohol 5 ml, and then dried at 100 °C in a muffle furnace. After that, on the basis of initial sample mass the fiberglass was impregnated with calculated amount of aqueous solutions of cobaltous nitrate salts and glycine. Figure 2 shows the sequence of producing steps of catalyst based on fiberglass [7].

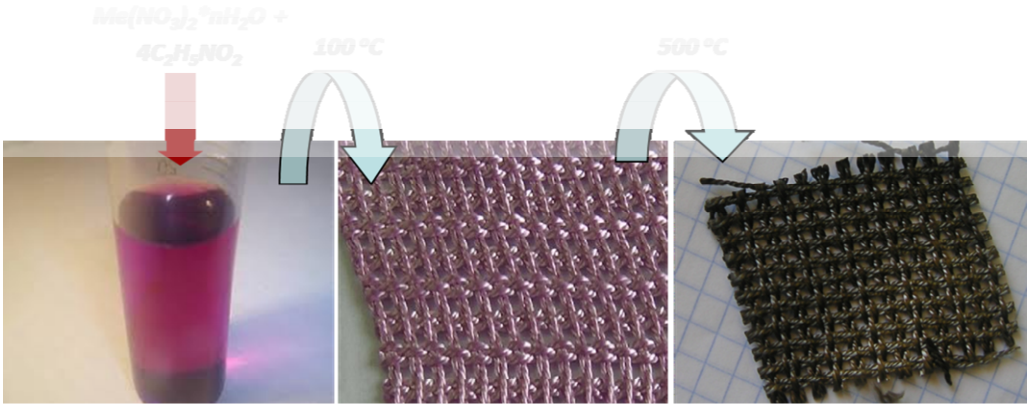
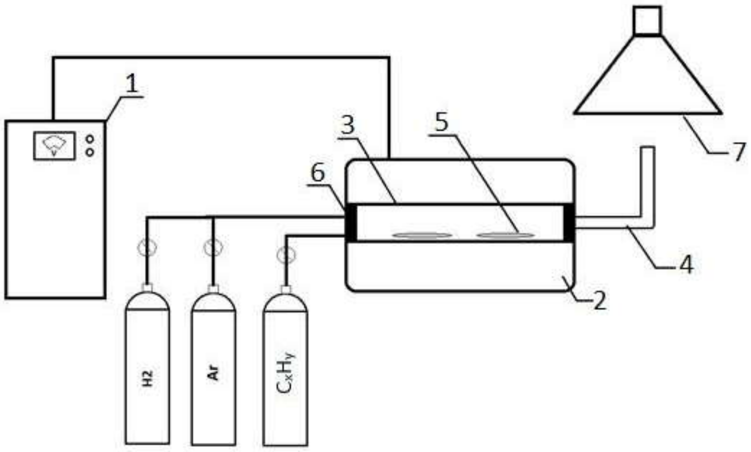


Figure 2 – The sequence of synthesis stages of metal oxide nanoparticles at fiberglass by solution combustion method [7]

Heat treatment in air provides additional oxygen molecules that required for the formation of metal oxide. The resulting metal oxide nanoparticles (cobalt, iron) are the catalysts for carbon nanotubes and nanofibers growth at the surface of fiberglass.

Synthesis of carbon nanotubes on glass cloth by chemical vapor-deposition method

Synthesis of carbon nanotubes was carried out in a tubular reactor consisting of flow type with one heating zone and quartz tubes. Figure 3 shows a setup for the synthesis of carbon nanotubes by chemical vapor deposition method from propane-butane mixture. The reactor is made of quartz tube, is closed on two sides by special plugs for leak tightness. The reactor was placed to the tube-type furnace with a temperature controller with peak heating up to 1100 °C. The furnace provides uniform heating of entire inner cavity of quartz tube. The gas mixture that is used for synthesis of carbon nanotubes is composed of argon and propane-butane mixture. When the catalyst was placed to the reactor, the quartz tube was purged with argon. Upon reaching the desired temperature in reactor the propane-butane mixture was supplied. On completing of synthesis time, the supply of propane-butane mixture is ceased. Before the rector reached a room temperature, the argon was supplied to the reactor. Gas flow rate: Ar –150 cm^3/min, C_3H_8 – C_4H_{10} – 150 cm^3/min. The synthesis temperature was - 770-780 °C, the synthesis time was - 20 minutes. Gas flow rate and synthesis temperature were determined experimentally and they are sufficient and necessary for the synthesis of carbon nanotubes on catalyst. Increased time of synthesis more than 20 minutes leads to the formation of amorphous phase of carbon, and degradation of carbon nanotubes properties [8].



1 - current transformer; 2 - reactor; 3 - quartz tube; 4 - a metal tube for exhaust gas; 5 - silicon substrate with a catalytic coating; 6 - caps; 7 - ventilation tube

Figure 3 – Schematic diagram of a setup for thermocatalytic synthesis of carbon nanotubes by pyrolysis of propane-butane mixture

Temperatures and synthesis conditions were obtained experimentally and are necessary and sufficient for synthesis of carbon nanotubes.

Results and discussions

The obtained samples of cobalt oxide nanoparticles have been studied by various physical and chemical methods of investigation.

X-ray analysis to establish the structure and composition of the obtained cobalt oxide was carried out. Figure 4 shows diffractiogramm for the ultradispersed particles of cobalt oxide.

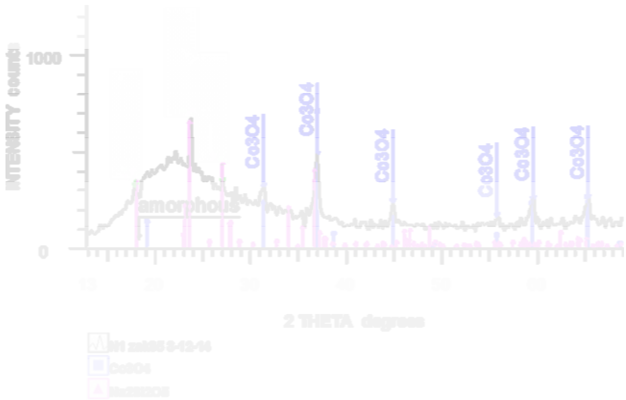
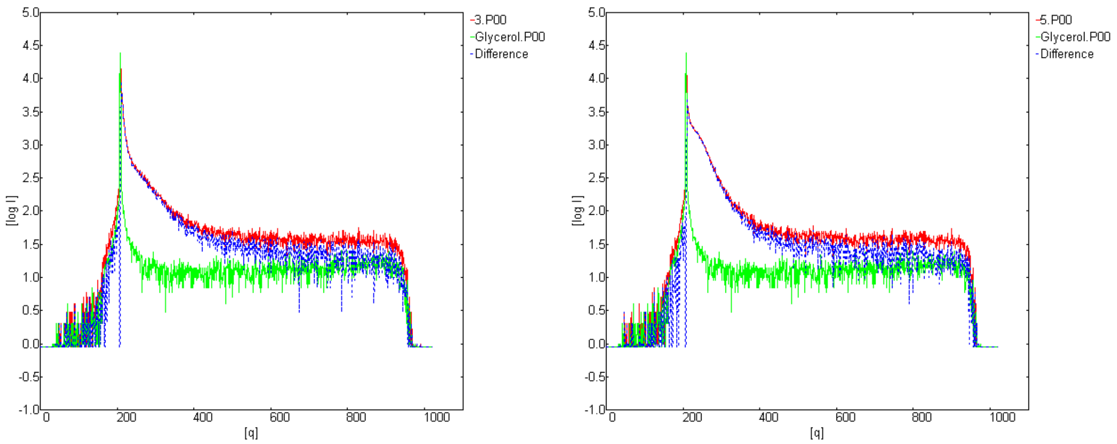


Figure 4 – The XRD patterns of ultradispersed particles of cobalt oxides, obtained by solution combustion synthesis

As seen from the diffraction pattern obtained in the synthesis of cobalt oxide nanoparticles have the formula Co_3O_4, according to the reaction:

$$3Co(NO_3)_2{\cdot}6H_2O + 6C_2H_5NO_2 + 6.5O_2 \rightarrow Co_3O_4 + 12CO_2\uparrow + 6N_2\uparrow + 33H_2O\uparrow.$$

To determine the effect of addition of nitric acid, experiments without the addition and with the addition of nitric acid in the initial mixture were carried out. The resulting samples were examined by small angle X-ray scattering. The glycerol was used as a template. Small-angle curves for glycerol and the nanoparticles of Co_3O_4 (φ=1, without the addition of nitric acid) and Co_3O_4 (φ=1, with the addition of nitric acid) (figure 5, 6). For determine the distribution of nanoparticles in size (on histogram is radius of the sphere) in the spherical approximation, the contribution of small-angle scattering of glycerol has been deducted from the curve.



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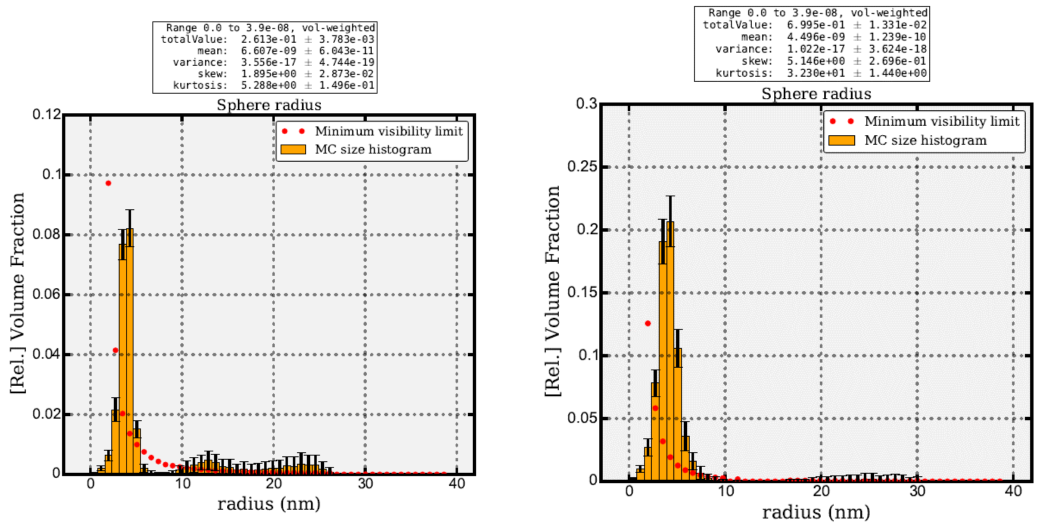
a) Co_3O_4 nanoparticles obtained without addition of nitric acid; b) Co_3O_4 nanoparticles obtained with addition of nitric acid

Figure 5 – Small-angle curves of glycerol and Co_3O_4 nanoparticles



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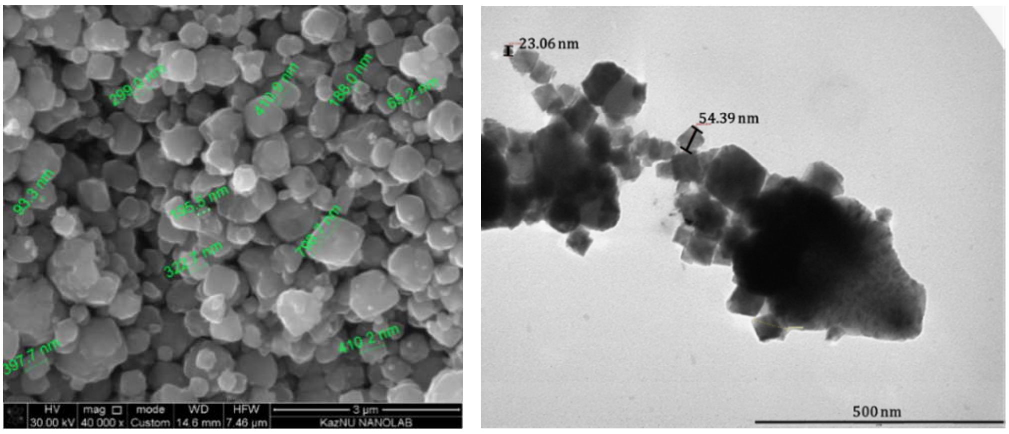
a) Co_3O_4 nanoparticles obtained without addition of nitric acid; b) Co_3O_4 nanoparticles obtained with addition of nitric acid

Figure 6 – The size distribution of Co_3O_4 nanoparticles

As seen from the graph of distribution of Co_3O_4 nanoparticles obtained without added nitric acid (figure 6) the bulk of particle has diameters 6-9 nm, there are also particles with diameters of 24-50 nm.

As seen from the graph of distribution of Co_3O_4 nanoparticles obtained with added nitric acid (figure 6) the bulk of particle has diameters 8-10 nm. In this example, all of the nanoparticles have a diameter of 16 nm and no particles of greater diameter. Obtained results showed that the addition of nitric acid allows obtaining more dispersed particles. In the case adding nitric acid formed nanoparticles with a small distribution of from 4 to 16 nm. Thus, nanoparticles, produced without the addition of nitric acid have a greater distribution from 4 to 30 nm. Further experiments for obtaining nanoparticles of cobalt oxides carried out with the addition of the nitric acid, since in this case the nanoparticles have higher dispersion.

Cobalt oxide nanoparticles, obtained at various ratios of the fuel and oxidant were investigated by a scanning and transmission electron microscopy. On the figure 7 is shown scanning and transmission electron microscope images of Co_3O_4 at the stoichiometric ratio of fuel and oxidizer (φ = 1).



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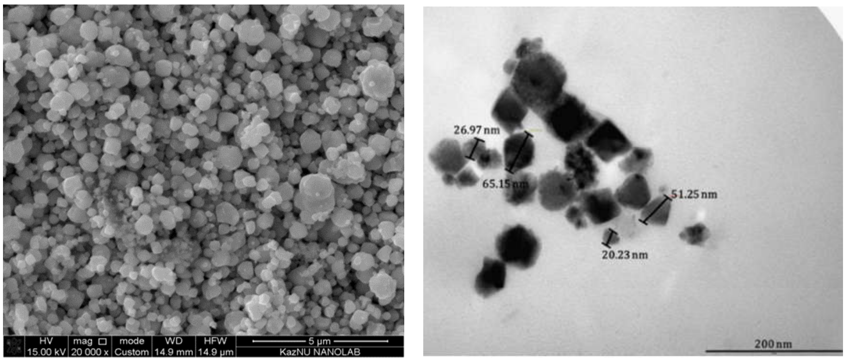
a) SEM image of Co_3O_4 nanoparticles; b) TEM image of Co_3O_4 nanoparticles

Figure 7 – Microstructure of nanoparticles Co_3O_4 at the stoichiometric ratio of fuel and oxidizer (φ = 1)

On the figure 8 is shown SEM and TEM images of Co_3O_4 at the stoichiometric ratio of fuel and oxidizer (φ = 1.5).



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a) SEM image of Co_3O_4 nanoparticles; b) TEM image of Co_3O_4 nanoparticles

Figure 8 – Microstructure of nanoparticles Co_3O_4 at the ratio of fuel and oxidizer (φ = 1.5)

As seen from the obtained pictures of scanning and transmission electron microscopes for particles of cobalt oxide at a stoichiometric ratio of fuel and oxidizer φ = 1, the particle size range from 23 nm to 60 nm, also agglomerates with size more than 500 nm are present. For particles of cobalt oxide at a ratio φ = 1.5 particle size ranges from 20 to 65 nm, without big agglomerates. A comparison of the two samples on the basis of SEM and TEM images, illustrates the positive effect of the addition of fuel above the stoichiometric ratio. Reaction between fuel and oxidant results in decomposition of the starting components to form gaseous products that lead to further dispersion of the final product.

The fiberglass based catalysts with active component in the form of metal oxide nanoparticles - the cobalt were used for the synthesis of carbon nanotubes by chemical vapor deposition method, is based on decomposition of carbon containing gaseous compound at high temperature. The glass cloth (the mass is 3-5 %) with metal oxide nanoparticles was used for the synthesis.

Carbon nanotubes at glass cloth with cobalt oxide nanoparticles have been investigated using scanning electron microscope to determine the structure and morphology of obtained one-dimensional nanomaterials at the surface of glass cloth as a result of synthesis.

Figure 9 shows SEM images of carbon nanotubes grown at the surface of class cloth with Co_3O_4 at different magnifications.

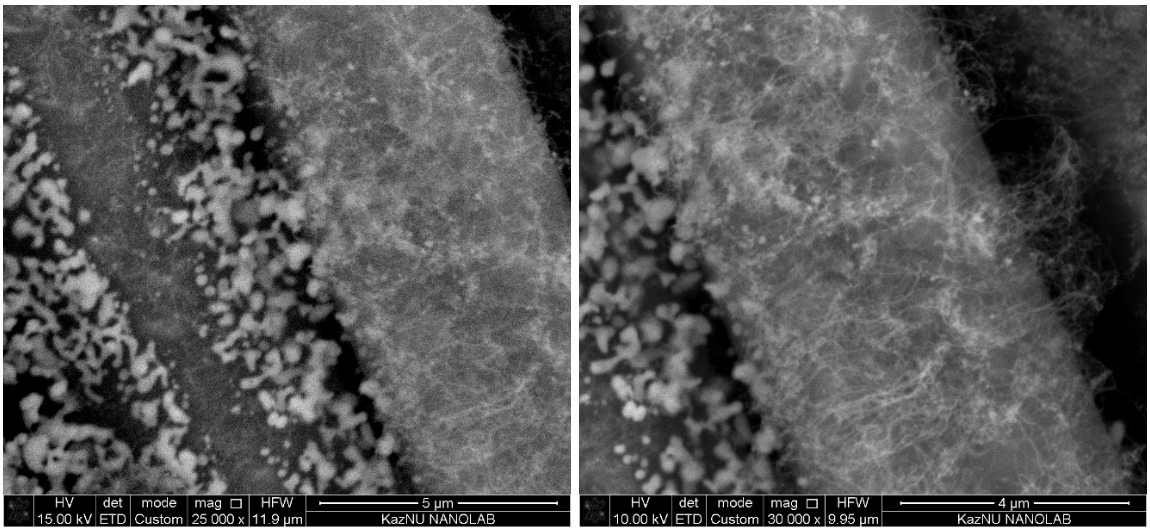

Figure 9 – SEM images of carbon nanotubes grown at the surface of fiberglass with Co_3O_4 at different magnifications

As can be seen from obtained images at the surface of glass cloth with Co_3O_4 the ultrafine particles of cobalt oxide are formed in large quantities, they are active centers of carbon nanotubes growth.

On the basis of obtained electroconductive smart textiles, the heated jacket for model of soldier has been made. For this purpose, the fiberglass sample with carbon nanotubes coating with an area of 24 cm^2 was equipped by two electrodes from copper wire and connected to the power source - the battery. For aesthetic appearance and shape the jacket from heat resistance material was sewn. Figure 10 shows the pictures of the soldier model with jacket based on conductive smart textile.

After manufacture of the model the approbation for heating effect at lower temperatures was made which is behavior modeling of obtained material under critical conditions. For this purpose, the sample was cooled to a temperature of 0 ^oC, at the same time the jacket is not connected to a power source, but after cooling the sample was connected to a power source. The sample temperature was measured by chrome-aluminum thermocouple with a digital temperature measurement sensor. Figure 10 shows the photographs of the model and dynamics of temperature change of the jacket before connecting of the jacket to a power source [9].

Figure 10 – Photos of soldier model with a jacket based on glass cloth with carbon nanotubes coating and dynamics of jacket temperature changes before the connection and after connection to the power source

Figure 10 shows that at connecting the jacket based on glass cloth with CNT to the power supply, the temperature is increased smoothly from 0 to 28 ^{o}C, 36 and 45 ^{o}C respectively. In this case, our goal is the preparation of heated jacket for clothing and outfit of people who are in critical to human body temperature conditions - soldiers, climbers, athletes, etc. The temperature of the heating jacket must be comfortable for the body and should not exceed a certain threshold. The obtained results showed that by varying the power supply it is possible to change the maximum heating temperature. In our case, the maximum temperature was 45 ^{o}C, which is sufficient for keeping of normal functioning of human body at low and negative ambient temperatures. High conductivity and thermal stability of the CNT-structures allows to provide high current carrying capacity. Thus, CNT-composite materials are perspective materials to creating a new type of electro-energy systems.

Conclusion

Cobalt oxide nanoparticles by the method of solution combustion was prepared. The influence of the ratio of the initial components on the particle size was investigated. without big agglomerates. Particles of cobalt oxide at a stoichiometric ratio of fuel and oxidizer φ = 1, the particle size range from 23 nm to 60 nm. For particles of cobalt oxide at a ratio φ = 1.5 particle size ranges from 20 to 65 nm, without big agglomerates. This method to deposit of Co_3O_4 nanoparticles onto glass cloth for synthesis of carbon nanotubes was used. Based of obtained textiles, the heated jacket for model of soldier has been made. The manufacturing method of flexible heating element based on glass cloth with the coating from carbon nanotubes was developed. This type of electrically conductive textile has shown a good Joule heating, and this factor makes it promising for a number of applications.

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