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Synthesis of CNT and CNT-Cu composites

Abstract. Nanostructured carbon materials feature unique properties and the expanding range of applications, so the research of methods for their synthesis is of high actuality. During the last years, even well-known CVD method of CNT synthesis was significantly modified and upgraded. In most of these advances, the uniformity of homogenous catalyst particles was concerned as the main goal. This paper presents results in the development of technological procedures for uniform deposition of catalysts from aqueous solutions of salts and electrodeposition with better CNT parameters.The water-soluble salts used were nickel nitrate and cobalt acetate. Degreased in organic solvents and cleaned with ultrasound the substrates were immersed in aqueous solutions of salts. Particles of metal oxides were formed while the sample was annealed in muffler at 400^{o}C in the air. Then CNT were synthesized in a quartz flow reactor in hydrogen at temperatures 650-700^{o}C in ethanol vapors. Raman spectra of so produced samples correspond to MWCNT. Ratios of I_D/I_G lines comprised 0.8-1.2. Electrodeposition of catalyst was used to improve the uniformity of CNT deposits. The deposition was from nickel nitrate solution with the addition of water-soluble polymer. One part of obtained samples was directly used for CNT synthesis. The second part was preheated at 400^{0}C in the air. CNTs were synthesized at 650^{0}C from ethanol vapor in 15 minutes. Revealed, that catalyst pre-heating in air leads to much more uniform CNT cover. At that, the quality of CNT is higher, such as ration I_D/I_G ~0.8. So the structural perfection is higher than in the case of a catalyst deposition from solution. Further electrolytic deposition of copper over CNT layer allowed obtaining CNT-Cu composite. SEM images show the morphology of so obtained composite as viewed from CNT side.
Key words: CNT, sol gel-method, electrodeposition, spin coating, ZnO, CNT-Cu composites.

Introduction

Carbon nanostructured materials such as carbon nanotubes (CNT), graphene, carbon fibers and based on them composites feature unique properties and a wide range of applications [1-3]. Therefore developments of synthesis methods for such structures are of high actuality. A good synthesis of CNT-based composites should have high uniform deposition of CNT, which demands uniform distribution of catalyst's particles, such as iron, nickel, cobalt. Given article describes improvements of sol-gel technique, methods of electrodeposition and spin coating for the production of catalyst particles and following synthesis of carbon nanomaterials and composites.

Sol-gel methods

Sol-gel method [4-6] was used for deposition of metal salts on a silicon substrate with the purpose to create catalyst particles as the points of CNT's growth. For that purpose,sol was made based on the solvent metal salts and a chelating agent. Water-ethanol mixture was used as a solvent; acetates were used as metal salts, water-soluble polymers and some amount of lactic acid were used to prevent aggregation. The sol was carefully mixed in magnetic stirrer during 3-24 hours.

For uniform deposition of thin films of metal salts over the flat silicon wafers we've used the procedure of centrifugation (spin coating), in which an excess amount of the sol solution is placed on a substrate which is then rotated at a high speed to uniformly spread the liquid across the surface of the substrate under centrifugal force. It is important to provide a uniform wetting of the substrate. The transparent sol solution was applied to the pre-degreased surface of a silicon substrate placed on the table, which was then rotated at about 2000 rpm for 2-3 minutes. Then the sample was dried in an oven at 110°C until the gel formation and then

placed for binding annealing in the air in a muffle furnace at about 500°C at which oxides are formed from the gel particles.

Synthesis of CNT was carried out by placing substrates in the synthesis reactor, sealing the reactor and heating-up in a hydrogen atmosphere at a rate of 6-7 degrees per minute. During the heating, metals are reduced from oxides so forming catalyst particles. The synthesis was carried out for 10 minutes in the ethanol vapor. Fig. 1 shows the surface morphology of the samples obtained in a single experiment on substrates which were deposited by sol-gel method catalyst particles. It is seen that the metal salt concentration in the initial solution plays an important role in getting the CNT layer. CNT layer is not continuous at low concentrations of salts in initial sol; instead at a higher concentration, the bundles of multi-walled CNT are formed. The optimum concentration for obtaining high-quality multi-walled CNTs is derived.

Hydrothermal method

We used the hydrothermal method to grow arrays of zinc oxide nano-rods on silicon substrates. SEM pictures of the original ZnO bars are shown in Fig. 2a. Then, by applying dilute ferric chloride solution to the substrate surface, followed by annealing, the oxide nanoparticles were obtained dispersed over the surface of nano-rods and having a high specific surface area. Such substrates have been used for the low-temperature synthesis of CNTs in a hydrogen atmosphere with ethanol vapor. CNTs of sufficiently high quality were obtained. Thus we advanced the method of hydrothermal synthesis to substrates with a high area and coated them with the catalyst particles to produce CNTs.

Electrodeposition

To create the catalyst's nanoparticles on the substrate surface we used an electrodeposition method. Electrolyte for the deposition was the mix based on an aqueous solution of metal salt, the surfactant Triton X-100. The ferrous sulfate (II) or nickel sulfate (II) were selected as the metal salts and sodium sulfate (Na_2SO_4) was used to increase electrolyte conductivity. The typical solution had a concentration of 0.05 M of nickel or iron sulfate and 0.5M of sodium sulfate; boric acid was added as a buffer for adjusting pH. The solution was thoroughly stirred on a magnetic stirrer for 3-24 hours and filtered before use.

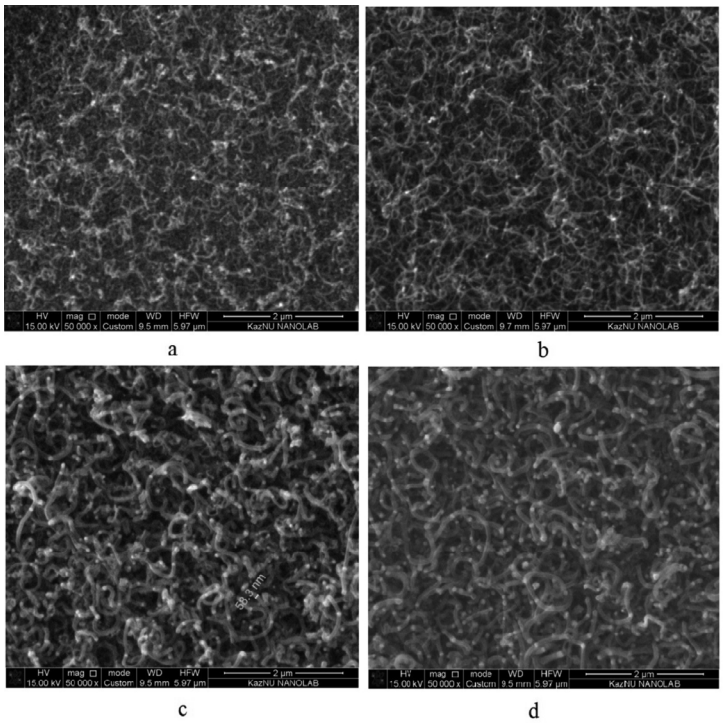


Figure 1 – CNT synthesized at 650°C on substrates with different concentration of sol: a) 0.0002 M; b) 0.0005 M; c) 0.001 M; d) 0.002 M.

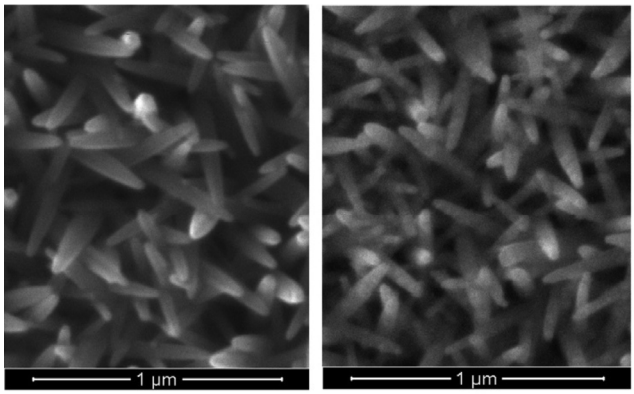


Figure 2 – Nano -rods of hydrothermally synthesized ZnO:
a) initial; b) with deposited nanoparticles of copper oxide, ready for CNT synthesis

Cathodic electrodeposition was performed using a stabilized current source-potentiostat Elins P-30J in the three-electrode configuration. As a working electrode, a counter electrode and a reference electrode were used, respectively, a silicon substrate, a platinum electrode, and a silver chloride electrode. The deposition was performed at a current of 10 mA/cm^2 and the deposition time was varied from 30 seconds to 10 minutes. Then, the substrate was pulled out and washed in water.

It has been found that an important process step is the oxidative annealing in air at 450-500°C. CNT synthesis is then carried out using substrates prepared as described above. Fig. 3 shows the morphology of the samples on the surface of CNTs substrates obtained by electrodeposition of catalysts, depending on electrodeposition process duration. It can be seen that the CNTs synthesized at certain parameters of the deposition process do not grow if electrodeposition was short (15-30 seconds), while the longer duration of electrodeposition (over 3 min) leads to catalyst particle size of 100-400 nm and to bundles of multi-walled CNT.

Electrospinning

Electrospinning method is one of the most effective methods to obtain carbon fibers and composites [7-9]. Synthesis of the catalyst nanoparticles by electrospinning is based on the use of polymer materials and mixtures of salts having carbon solubility. With electrospinning it can be easily achieved, that small amounts of metal salts will be very uniformly distributed over the length of the fibers in the polymer. During the subsequent heat treatment of fibers under specific conditions, the metal oxides can be formed with simultaneous destruction of the carrier (polymer), providing that the oxides are not aggregated into larger particles, and are formed with nano-size distribution close to monodisperse one.

The polymers we used in experiments were: polyvinyl alcohol (PVA), polyvinyl pyrrolidone, polyvinyl acetate (in some cases). Salts of metals such as nickel acetate, cobalt, copper, nickel and iron nitrates and others were used to form the catalyst nanoparticles.

Fig. 4 shows SEM image of composite fibers immediately after synthesis (a) and after annealing in air at 250°C for 2 hours, followed by reductive annealing in hydrogen (250°C, 2 hrs). As it is seen from the picture, the nanoparticles formed after annealing are of average diameter near 50 nm with a small spread. Actually, it was possible to control the nanoparticle sizes in a wide range varying the concentration of the initial solution of polymer and salt. The polymer itself collapses and evaporates during annealing in an oxidizing atmosphere.

It has been found also that is necessary to keep a low rate of heating during the fibers anneal to form oxides nanoparticles (about 1-3 degrees per minute). In this case, the polymer degradation process runs at an optimal speed, and if polymer fibers are uniformly covered with metal salts they are retaining their shape while gradually thinning, and oxide particles are formed with a small spread in size. In the case of higher heating speed (8-10°C per minute) we observed twisting and deformation of the fibers, and polymer melting, which leads to adhesion of the material and to a larger amount of coarse particles with the formation of oxides inclusions.

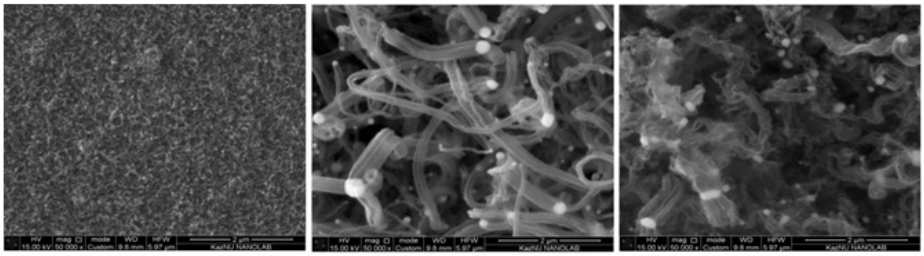


Figure 3 – CNT synthesized at 650°C on the substrates with the electrodeposited catalyst depending on electrodeposition duration: a) 15-30 seconds; b) 3 minutes; c) 10 minutes.

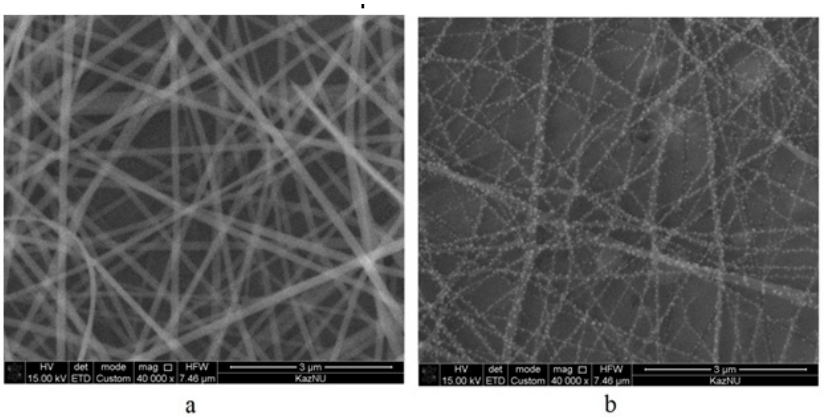


Figure 4 – Composite fibers PVA+AcNi: a) after synthesis; b) after annealing in hydrogen. The vacuum heat treatment allows producing nanoparticles with an average size of 20 nm, as shown in Fig. 5, and the fibers do not dissolve, as it happens during annealing in an oxidizing atmosphere, but became graphitized.

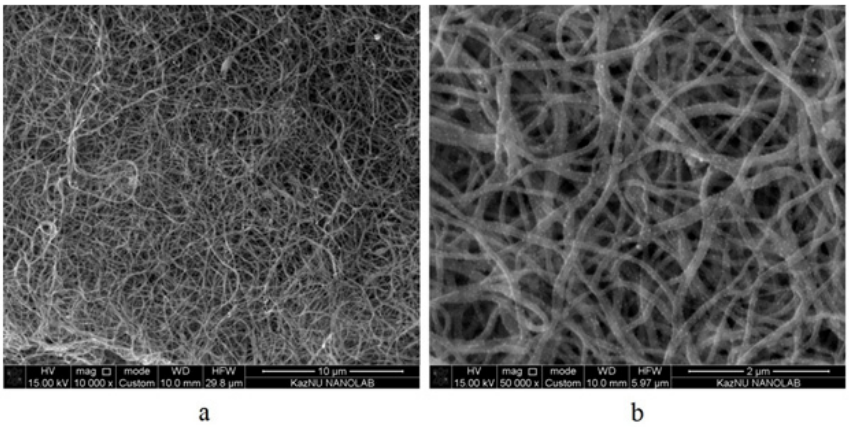


Figure 5 – Composite fibers: a) initial; b) after anneal at 500°C in vacuum.

Figure 6 shows Raman spectra of annealed fiber with catalytic nanoparticles and Raman spectra of CNTs samples obtained by using these fibers as substrates for the CNT synthesis at 650°C in a mixture of hydrogen and ethanol vapor (as the carbon source). As it can be seen from the figure, the Raman spectrum of the annealed fiber (curve 1) is close to the spectrum of amorphous carbon. Curve

2 corresponds to CNTs grown on the annealed fibers. According to the literature, the spectrum corresponds to the multi-walled CNTs. As can be seen from Fig. 6, the spectrum intensity of the D band is lower than the band G, and sufficiently high intensity of 2D peak is observed. This evidences the high quality of the nanotubes.

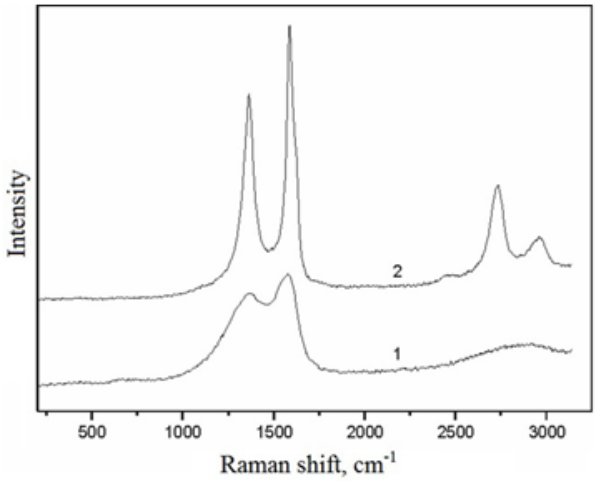
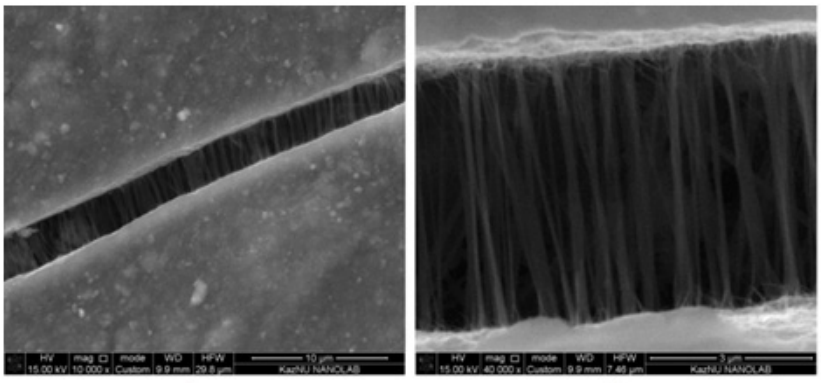


Figure 6 – Raman spectra of fibers after vacuum anneal of PVA polymer at 500°C (curve 1) and of CNT's synthesized on these fibers at 650°C in ethanol vapors (curve 2).

CNT-Cu composites

Application of CNT (for hydrogen storage, for example) requires that CNT should be not just a powder but compacted as a composite film (for instance) which can sustain higher temperatures and allows hydrogen permeation. Such a composites could be created binding CNT to metals. In our work the composite of SWCNT with copper was created using copper electrodeposition over CNT layer. Since we synthesized SWCNT over paper filter it is convenient to use it as a dielectric separator between CNT layer (cathode) and copper (anode). The copper was electrodeposited on CNT layer from electrolytic solution (0.5MCuSO4 + 0.2M H2SO4) at low density of current during about two hours. Fig. 7 shows the morphology of the composite we've prepared by deposition of copper over the layer of CNTs, a view from the CNT layer. The CNT layer was obtained from electrodeposition and appears as nonstructural, however, if the sample is bent enough to start cracking, the appeared surface cracks are filled with stretched nanotubes, which can be clearly seen in the Fig. 7. Raman spectrum of CNT-Cu composite corresponds to the spectrum of multi-walled CNT. Thus, electrolytic deposition of copper on the conductive layer of CNTs has allowed obtaining composites based on CNT and a copper.



a b

Figure 7 – Front side (a) and the area of rupture (b) of CNT-Cu composite

Conclusion

The sol-gel method, hydrothermal method, electrodeposition and electrospinning were refined with the purpose to form better catalyst nanoparticles and the subsequent synthesis of carbon nanotubes and composites based on them. The structural properties and morphology of synthesized CNT samples, depending on the technological conditions of synthesis were studied. CNT-Cu composites were synthesized based on carbon nanotubes and a deposited copper layer.

Acknowledgements

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