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Preparation and characterization of catalyst mix Fe-Co/MgO for carbon nanotubes growth

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Fe-Co/MgO is one of the most common catalyst mix applied to carbon nanotubes (CNTs) growth in chemical vapor deposition process. Therefore, here we present detailed study on the preparation and characterization of Fe-Co/MgO. The precursors of Fe and Co are iron (II) acetate and cobalt acetates, correspondingly. The molar ratio of the catalyst mix is Fe:Co:MgO=1:1:100. Initially, thermogravimetric analysis (TGA) of the mixture was performed. TGA analysis of it indicated the stepwise mass losses which pointed out the crucial thermal conditions for the changes in the elemental composition, morphology, crystallographic structure and vibrational properties. In current state of the art the lowest growth temperature for singlewalled carbon nanotubes is 550°C in CVD technique and here the characterization of the catalyst mix strongly suggest that this temperature can be decreased what would enhance the compatibility of CNT growth with current complementary metal-oxide-silicon (CMOS) technology for CNTs-based nanoelectronics. The morphology, crystallographic structure, elemental composition of the samples and its spectroscopic properties were performed via high resolution transmission electron microscopy (TEM), X-ray diffraction (XRD) and Infrared spectroscopy (IR), respectively.

Keywords: catalyst, thermogravimetric analysis TGA, chemical vapor deposition CVD, carbon nanotubes.

INTRODUCTION

Since the discovery of carbon nanotubes (CNTs)[1], a number of researches have been made because of their unique physical and mechanical properties which lend themselves to a variety of applications, such as field-emission displays[2], polymer composite materials[3], sensors[4] and elements of new logic circuits[5]. CNTs have been produced using various approaches, such as arc discharge method and, laser ablation, and chemical vapor deposition (CVD)[6 - 9]. Synthesis of CNTs using CVD method has attracted much attention because of many advantages such as high purity, high yield, controlled growth. Additionally, this technique is very promising in its application in CNTs-based electronics, where low temperature growth of tubes is required. Each method requires the application of the catalysts for the CNTs growth. So far the most effective catalysts for the CVD growth of CNTs are known to be iron (Fe), cobalt (Co), and nickel (Ni)[10]. The peculiar ability of these metals was suggested to relate to the catalytic activity for the decomposition of carbon precursors, the formation of meta-stable carbides, the diffusion of carbons, and the formation of graphitic sheets, etc.[11]. Despite tremendous progress in synthesis of CNTs, the systematic study on the catalyst characterization is not much reported so far.

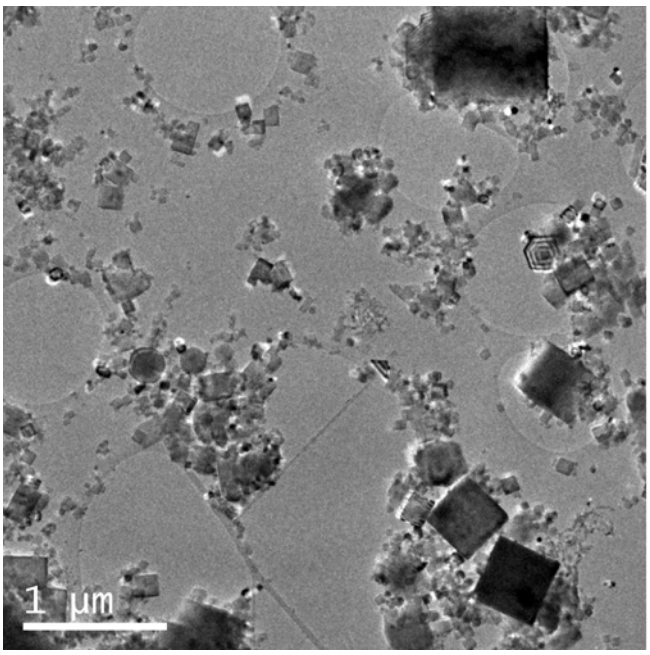
In this work we present detailed study on the preparation and characterization of Fe-Co/MgO before introduction the carbon feedstock in CVD synthesis of CNTs of the CVD. Firstly, TGA of the catalyst was measured. TGA analysis of it indicated the stepwise mass losses which pointed out the crucial thermal conditions for the changes in the elemental composition, morphology, crystallographic structure and vibrational properties.

EXPERIMENTAL

The catalyst mix was prepared as follows: a mixture of butanol, cobalt acetate, iron acetate and magnesia oxide, (Co:Fe:MgO= 1:1:100) were dispersed for 1 h in an ultrasonic bath at room temperature. Afterwards, the mixture was dried on a hot plate at 150°C using a magnetic stirrer for 30 min and subsequently, the resultant product was grounded in a ceramic mortar to form a homogeneous catalyst precursor mix in powder form. 15 mg of the catalyst powder was placed into a ceramic crucible. Next, it was introduced to the thermogravimetric analyzer to be evacuated ($\sim 10^{-2}$ mbar) and then heated at the temperature of 850°C with the temperature ramp 10°C/min. TGA analysis of it indicated the stepwise mass losses. After analysis of TGA and DTA data, 20 mg catalyst powder mixture was heated at different temperatures (160°C, 240°C, 310°C, 375°C and 410°C) for 30 min, in order to evaluate the changes in the catalyst occurring before the nanotubes formation. The morphological studies of the catalyst samples were conducted on a high-resolution transmission electron microscope (HRTEM) – FEI Tecnai F20, energy dispersive X-Ray spectroscopy (EDX). The XRD studies were carried out on the Philips X'Pert PRO difractometer. The following parameters of XRD measurement were applied: Cu Kα, high voltage 35000 and current 0.03 A. 0.05 degree step and 3 second counting time per step for the purposes of phase analysis were applied. The X'Pert High Score program with the ICDD base to the phase analysis was used. The presence of functional groups was verified with the aid of Infrared spectroscopy (IR, Nicole 6700) in a spectral range from 4000 to 400 cm^{-1}.

RESULTS AND DISCUSSION

In order to determine the thermal changes in the as-produced catalyst mix TGA analysis was performed. The



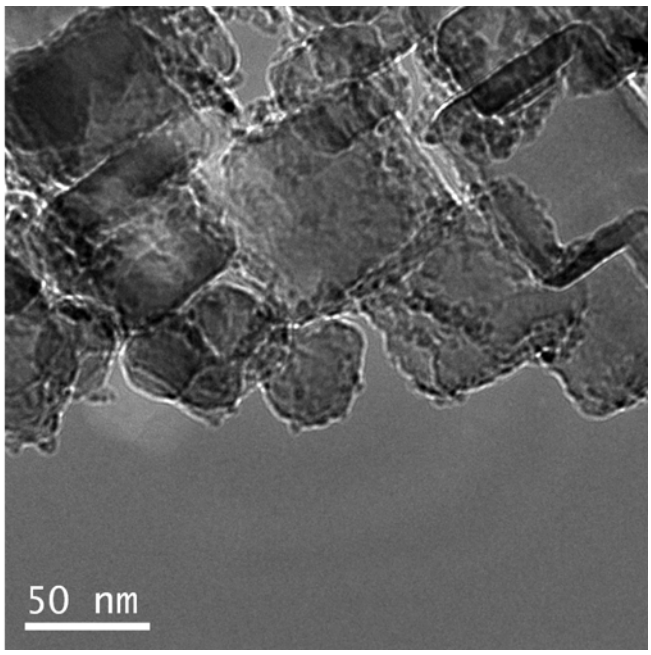


Figure 1. TEM images of the catalyst calcinated at 410°C

temperature range was between room temperature until 850°C. 850°C is a typical temperature applied for the synthesis of carbon nanotubes using this catalyst. From DTA graph one can observe that the main mass losses occurred at ca 100°C, 210°C, 285°C, 360°C, 390°C .Thus, five samples of the catalyst mix heated to the temperatures slightly exceeding the above-mentioned values were prepared. The exact annealing temperatures were following: 160°C , 240°C , 310°C, 375°C, 410°C. These values were sufficiently high for the thermal changes occurred for each step related to the mass loss observed in TGA analysis. Therefore, the labels of the prepared samples are described following: **A-r.t.** (room temperature) and heated samples – **A-160**, **A-240**, **A-310**, **A-375**, **A-410**. Each sample was annealed for 30 min.

Figure 1 presents TEM images of Fe/Co/MgO catalyst calcinated at 410°C, where typical cubic shape MgO particles are observed. The average size distribution of substrate particles was calculated to be between 30 and 110 nm. The darker islands in the MgO cubes are attributed to the presence of catalyst alloys with the mean size estimated around 4 nm are visible on the substrate surfaces (see right panel).

Figure 2 presents IR spectra of reference sample (A-r.t.) and heated samples A-410. IR response of A-r.t. sample exhibits peaks at 850 cm^{-1}, 1020 cm^{-1}, 1420 cm^{-1}, 1480 cm^{-1}, 1550 cm^{-1}, 3700 cm^{-1} which are assigned to CH, CO, CH_2;CH_3, OH respectively. The increase of the annealing temperature results in the decrease of the intensity of some of the modes. This can be clearly observed for three vibrations at 1420 cm^{-1}, 1480 cm^{-1}, 1550 cm^{-1}. Finally, both of the peaks vanish and only weak mode at 1420 cm^{-1} for the sample heated at 410°C remains. This observation indicates that these thermal conditions are efficient for the removal of -OH groups from the catalyst mix. IR of the final product heated at 410°C shows only two weak modes at 850 cm^{-1} and 1420 cm^{-1} which means that at this temperature almost all the peaks being related to the presence of carbon-containing functional groups are eliminated.

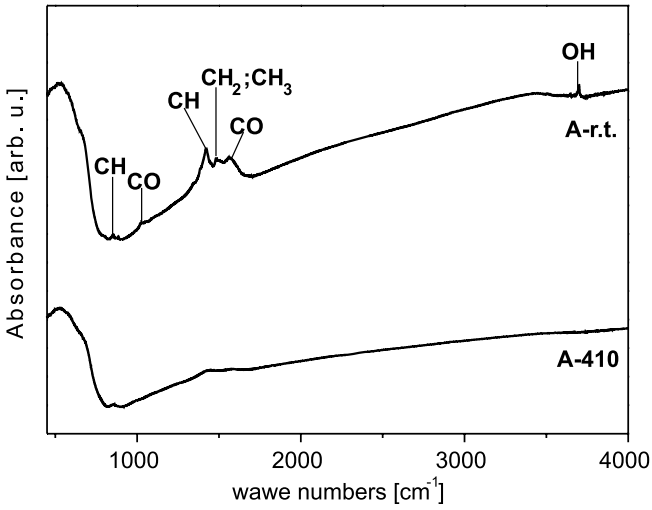


Figure 2. IR spectra of the catalyst samples A-r.t. and A-410

Now we turn to the analysis of the crystallographic structures of the samples (Figure 3). The main phase was assigned to the MgO (* symbol), the are also some small amounts of $Mg(OH)_2$ (**x** symbol) and $Mg_4(OH)_2(CO_3)_3$*$3H_2O$ (**o** symbol). After treatment at 240°C the $Mg_4(OH)_2(CO_3)_3$*$3H_2O$ phase decomposed to MgO. The Mg(OH)2 phase decomposed partially to MgO after being annealed at 240°C and completely after 310°C. The FWHM (Full width at half maximum) of MgO (111) does not change with the heat treatment at 410°C what means that the average size of MgO crystals remain unchanged upon the annealing procedure.

The above described data show the morphological, crystallographic and vibrational characterization of the catalyst mix which can be possibly used for the carbon nanotubes synthesis. Despite the promise of nanotubes grown by CVD, the high growth temperature (>800°C) of CNTs is a barrier for nanodevice fabrication. The lower growth temperatures strongly increase the compatibility of CNT growth with current complementary metal-oxide-silicon (CMOS) technology for CNTs-based electronics., plasma enhanced chemical vapor deposition (PECVD) has been recently applied for synthesis of nanotubes at

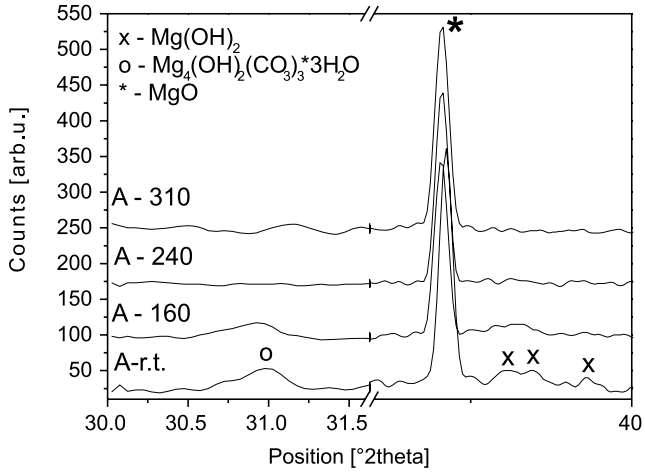


Figure 3. XRD powder pattern of the powder catalysts before the heat treatment

lower temperatures[12 – 15]. Unfortunately, the nanotubes produced at lower temperatures by PECVD are mainly multiwalled carbon nanotubes (MWNTs)[12 – 13]. Using the microwave plasma chemical vapor deposition method, MWNTs were grown at ~450°C by Wilson and co-workers[13]. To the best of our knowledge, the lowest growth temperature for SWNTs is 550 C in CVD technique[14]. They used zeolites as a supporting template for the Fe/Co catalyst. In our previous study this mixture was applied for the synthesis of carbon nanotubes at minimal thermal conditions of 850°C with methane and ethanol as carbon feedstocks[16 – 17]. Performance of this systematic analysis on the formation of Fe-Co/MgO mix gives the chance to find the optimal conditions for the low temperature synthesis of singlewalled carbon nanotubes. Therefore, more experimental studies are currently in progress.

CONCLUSION

The presented study shows that the final product of the catalyst mix Fe-Co/MgO is obtained already at 410°C which was supported via TGA/DTA analysis. HR-TEM and its EDX mode revealed the MgO cubical shaped structures with the average size of 60 nm and the elemental composition: Mg, O, C, Fe, Co, respectively. XRD patterns confirmed the MgO with embedded catalysts is the phase which could take part in the carbon nanotubes nucleation. Finally, we believe that this catalyst mix can be used in carbon nanotubes -based electronics. However, more experimental work has to confirm it.

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