

## SYNTHESIS OF VERTICALLY ALIGNED ARRAYS OF MIXED SINGLE-MULTI WALL CARBON NANOTUBES BY CVD METHOD WITH THE VOLATILE CATALIST.

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More research - more unusual properties Carbon Nanotubes (CNTs) are demonstrating. Special curiosity are exiting a Single Wall Carbon Nanotubes (SWCNTs) because the specificity of their properties and huge variety of their applications. SWCNTs should be produced of high quality, in large quantity, with the accepted prize and the given geometry (diameter and length).

The main methods of the CNTs synthesis are: arc discharge, pulsed laser ablation and chemical vapor deposition (CVD).

In most cases SWCNTs are obtained by the arc discharge and laser ablation. These methods do not satisfy the above requirements. By use of them the disordered bundles of SWCNTs of non standart length and diameters are obtained. Equipment and technology of their realization are very costly. The additional prize should be paid for the CNTs bundles cutting to the commonly used short specimens.

For the Multi Wall Carbon Nanotubes (MWCNT) synthesis CVD method is mostly used. This method ensures the synthesis of the arrays of vertically aligned MWCNTs and in general satisfies the above requirements.

The aim of the present investigation is to find the conditions of CVD method realization at which the arrays of vertically aligned SWCNTs would be synthesized at least in the combination with the MWCNTs.

The atmospheric pressure CVD method of CNTs synthesis was realized by the high temperature pyrolysis of fluid hydrocarbon (p-xylene [ $C_8H_{10}$ ]) in the presence of volatile catalyst (ferrocene [ $Fe(C_5H_5)_2$ ]) with the use of Ar as a gas-carrier. The aerosol of the solution: fluid hydrocarbon- volatile catalyst was delivering into the synthesis zone by the dosed injection. The advantage of the injection process is that it ensures the possibility to vary in wide range the type of hydrocarbons, percentage content of the catalyst in the solution, do not require to preliminary form the nanostructured clusters-catalysts on the surface of the substrate. This process is characterized also by low energy consumption and non toxicity of the initial reagents.

The synthesis process was realized in the tubular type quartz reactor of the specially constructed equipment.  $SiO_2$  substrate was used. Reactor was heated to the temperature of 850°C in Ar atmosphere (Ar flow rate-1000cm<sup>3</sup>/min). After the one minute of process duration reactor was cooled up to room temperature. A series of experiments were carried on with the variation of the ferrocene percentage in solution (1,0%-10%) injected into the Ar flow.

As SEM and TEM analysis showed in this regime of CNTs synthesis the arrays of tightly packed MWCNTs with the inclusion of the ordered bundles of SWCNTs were obtained. The structure of CNTs with 1,0% (specimen 1) and 10% (specimen 2) of ferrocene in solution was identical. The outer diameter of MWCNTs was in the range of 20-30 nm and

the diameter of SWCNTs – in the range of 1-3 nm. The height of the arrays (the length of CNTs) is some dozens of micrometers.

Raman spectra of the specimens 1,2 contain three picks. Pick in the range of  $1580\text{ cm}^{-1}$  (G-line) corresponding to the twice degenerated deformation oscillations of the hexamerous ring in  $E_{2g}$  electronic configuration of  $D_{6h}^4$  crystal symmetry. This testifies to the presence of carbon in the form of ordered hexagonal lattice. It might be grafen, SW or MW CNTs. Second pick in the range of  $1360\text{ cm}^{-1}$  (D-line) corresponds to vibration state of the ruinous hexagonal lattice near the crystals boundary and witnesses the presence of the not fully ordered transition forms of carbon (milled graphite, soot, another carbonized substances).

The ratio of the intensities  $I_G/I_D$  characterizes qualitatively the structure of synthesized CNT arrays: higher this ratio - higher quality of CNTs. In the case of specimen 1 the ratio  $I_G/I_D = 1,08$  (Fig. 1a), but in the case of specimen 2 the ratio  $I_G/I_D = 0,70$ . It means that in the case of 1,0% of ferrocene in solution CNT arrays contain less of ruinous forms of carbon than in the case of 10% i.e. the smaller concentration of catalyst in the array - the higher quality of CNTs.

The presence of pick in the low frequency spectrum range - Radial Breathing Mode (RBM) testifies to the presence of SWCNT in the arrays. More over it contains the characteristic information on SWCNTs structure according to the expression  $\sqrt{(\text{cm}^{-1})} = 6.5 + 223.75/d, 9+235/d$  where  $\sqrt{\phantom{x}}$  is the frequency of the radial modes of the oscillations of the SWCNTs hexagonal lattice and  $d$  is the SWCNT diameter in nanometers. Using this expression  $d$  was calculated. In both cases of specimens 1 and 2 the presence of SWCNT is observed. In the case of specimen 1  $\sqrt{\phantom{x}}=183,1\text{ cm}^{-1}$  and calculated value of  $d$  is equal to 1,2 nm. In the case of specimen 2  $\sqrt{\phantom{x}}=132,9\text{ cm}^{-1}$  and calculated value of  $d$  is equal to 1,8 nm. So Raman spectroscopy showed qualitatively the presence of carbon in different forms in the CNT arrays and quantitatively gave the possibility to reveal SWCNTs and to calculate their diameter.

The results of thermogravimetric analysis (TGA) are presented by typical TG and differential TG of CNT arrays of specimen 1 and specimen 2.

TG indicates that in a case of specimen 1 it starts burning near  $545\text{ }^\circ\text{C}$  and ends burning near  $615\text{ }^\circ\text{C}$ .

In a case of specimen 2 it starts burning near  $594\text{ }^\circ\text{C}$  and ends burning near  $650\text{ }^\circ\text{C}$ .

The burning temperature of CNTs is related to the number of walls, quality of nanotubes, presence of catalyst and even bundle size in the case of SWCNTs. High burning temperature indicates high crystal quality. The increase in burning temperature was attributed to the formation of bundles and removal of catalyst.

It was estimated that unburned mass in boss cases less than 2% and may include ferrous particles This value is quite low, so CNT arrays synthesized by our method are pure enough to be used in different applications without purification process.

Differential TG curve revealed two picks ( $545\text{ }^\circ\text{C}$  and  $615\text{ }^\circ\text{C}$ ) in the case of specimen 1 and ( $594\text{ }^\circ\text{C}$  and  $644\text{ }^\circ\text{C}$ ) in the case of specimen 2. Different picks correspond to the different burning temperatures of CNTs. First pick is attributed to CNTs with the small number of walls up to single-wall. Second pick is conditioned by the majority of multi-wall nanotubes in our CNT arrays.

So thermographic measurements of the obtained CNT arrays showed that they consist of two major components - SW and MW CNTs.

By both methods – Raman spectroscopy and thermogravimetric analysis it was shown that in the case of SW/MW CNT arrays more that 70% are SWCNTs