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Multiwalled Carbon Nanotubes and Nanofibers: Similarities and Differences from Structural, Electronic and Chemical Concepts; Chemical Modification for New Materials Design

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Abstract – Multiwalled carbon nanotubes with cylindrical and conic morphology as well as nanofibers were rivised from structural, electronic and chemical viewpoints. After chemical modification by carboxyl groups they were used for linkage with bio-active compounds via aminogroups, implantation to polymeres and latex films, as support for calalitically active transition metals nanoparticles stabilisation.

The manifold of application spheres for the materials based on multiwalled carbon nanotubes (CNT) causes the increasing interest of the researchers to these objects. Several structures can be realized for carbon nanotubes and one of them is conic, where graphite layers form ca. 33º angle with tube axis. Differences between conic and cylindrical CNTs and classic carbon nanofibers (fig.1) can be pointed out from structural (XRD, electron diffraction, pore size), electronic (Raman spectrum, gas adsorption) and chemical (typical reactions) viewpoints independently from the way of theirs synthesis. X-Rays diffraction show that the typical line for most of carbon structures (002) is shifted to the greater angles in the following sequence: graphite, nanofibers, conic CNT, classic CNT. This fact witness that atomic distance goes down in this line and is in good agreement with electron diffraction data. The burning temperatures goes up from 430°C for nanofibers and 475°C for conic CNTs to 485 OC for classic one. The pore sizes distribution is quite narrow in the case of classic and conic CNTs (3-8 nm), while for nanofibes this parameter belongs to the interval 3-17 nm. In the Raman spectrum conic CNTs are more close to nanofibes due to the high intensity of the D-line and D/G line ratio, but this fact can be easily explained by their structure, namely by the passage of graphite layers to the surface with following damage of sp2 hybridization of the terminal carbon atoms. Thus, the experimental data show conic CNTs are more close to classic CNTs than to nanofibes with almost disordered graphite layers in the structure.

The development of new effective selective adsorbents for organic compounds and ions, materials for physiologically active compounds delivery, functionalized polymers, new catalysts, etc. are impossible without preliminary functionalization of carbon nanotubes by carboxyl groups, which, also, opens ways to their subsequent modification with different functional fragments: fluorescent, biologically active, biopolymer and others. All the experiments mentioned after can be made for both classic and conic CNT since nanofibers can be easily decomposed after such treatment. Experimental included synthesis of the carbon nanotubes doped by the transition metals, carboxylation of MWCNT by treatment in the mixture of strong mineral acids, characterisation of the products. The degree of functionalization can be determined by thermogravimetry with mass-spectral analysis, 13C NMR spectroscopy, fluorescent spectroscopy (with tagged group) and titrimetric analysis. Hereat TG-MS and NMR methods gives the total value of the contents of carboxyl groups in the sample, while fluorescent and titrimetric techniques makes possible to determine only amount of surface ones. Depends on the properties of the target material carboxylated MWCNT can be strongly sonicated with easily decomposing salts of catalytically active metals for obtaining of bonded depositing metal nanoparticles (3-8 nm) for utilization in catalysis; or treated for transformation of carboxyl groups to hydroxymethyl, chlormethyl, chloranhydride groups for immobilization of substituted amines for nano-bio interface development, or dispersed with surfactants in solvent for further implantation to polymer matrix or involved in reaction media during polymerization process for the same idea or modified by different organic compounds. The materials obtained have been carefully investigated by SEM, HRTEM, IR-,UV-VIS and Raman spectroscopy as well as luminescent, ^{1}H and ^{13}C NMR spectroscopy, thermal analysis and mass-spectrometry.

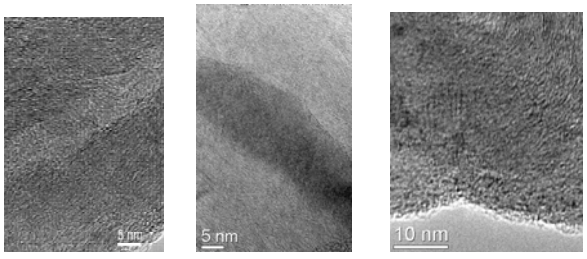

Figure 1: Conic and classic structures of MWCNT, nanofibres.