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Hybridization of natural inorganic materials (natural minerals) by carbon nanotubes

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Abstract:
In this work we briefly summarized results of extensive experiments focused on hybridization natural inorganic substrates by carbon nanotubes (CNTs). The kernel of the experiments is catalytic synthesis of CNTs on/into natural inorganic substrates involving two technological processes. The first one is incorporation of catalytically active metals into the structure of the substrates while the second one is in-situ synthesis of CNTs in a HF CVD reactor. The main objective of the experiments is to contribute to understanding the mechanism of the rise of new hybrid materials. Selection of the natural inorganic substances includes a group of minerals with similar chemical compositions but with markedly different morphologies as well as materials containing iron - colloid scraps after raw mineral mining. The main methods of characterizing the hybrids are Raman spectroscopy along with scanning and transmission electron microscopies.

Key words:
Carbon nanotubes, natural inorganic material, Raman spectroscopy.

INTRODUCTION

Nanocomposites with carbon nanotubes (CNTs) are investigated in many laboratories [1-3]. The reason is that CNTs have brought completely new material engineering due to their extraordinary electrical, thermal, mechanical and sorption properties. The properties of CNTs have been of interest since their discovery at the beginning of the 1990s [4]. Carbon nanotubes are macromolecules consisting of sp^2 hybridized atoms. The diameter of CNTs varies from 1 to 5 nm in single-nanoparticle nanotubes up to several tens of nm in multi-layer nanotubes. The length of one CNT can be several µm, or up to several centimetres.

A necessary condition for synthesis nanomaterials based on carbon nanotubes is the choice of substances containing any of the catalytically active metals or the presence of the catalyst. The most commonly used metals are Fe, Co, Cr, Ni, Pd, Cu, Ag, Au, Rh, Al, Mn, Zn, Mo and Ru and various nanoparticle combinations [5-7]. The catalytic effect is the conversion of sp^3 hybridized carbon into the precursor (e.g., methane) to sp^2 hybridized carbon in the nanotube structure.

The substances for hybridization by carbon nanotubes may be artificially prepared materials, the second group are of natural origin. There are several reasons for using natural inorganic materials for synthesis of CNTs. The first reason is that various separation techniques allow obtaining such ingredients that compete in homogeneity with synthetic substances. Another reason is a significantly lower price in comparison with synthetic materials and a high variability of structures and properties of the natural inorganic materials.

Potential applications of nanocomposites based on carbon nanotubes are in catalysis, nanoporous filters, fire refractory materials, flame retardants, selective adsorbents, and in special applications where carbon nanotubes have the function of a fortification component [8-15].

EXPERIMENTAL

In our study, the catalytic synthesis of hybrid nanomaterials involved the following technologically important steps.

- Separation of monomineral samples of selected types of natural inorganic materials from their source minerals.
- Separation of natural colloid materials containing catalytically active metals from the scraps after raw mineral mining.
- Incorporation of catalytically active iron on the surface or into the structure of the inorganic substrates. The main method is deposition from aqueous solutions of ferrous salts, e.g., $Fe(NO_3)_3$. By spin-coating we have solved the problem of

inhomogeneous distribution of catalyst particles on inorganic matrices.

- Synthesis of CNTs on the created substrate in the hot filament chemical vapour deposition (HF CVD) reactor, utilizing our optimized technological scheme.

We prepare nanocomposites directly in situ in the reactor. In HF CVD, hot tungsten carbide filaments are used as a source of energy that are placed in vacuum above the substrate. Non-conducting substrates must be masked by a metal. The deposition conditions are optimized by modifying the voltages, flow rates of gases (methane and hydrogen), temperature and time of synthesis. The working atmosphere was a mixture of methane and hydrogen. The precursors are activated by five filaments heated up to 2200 °C. The pressure and temperature during deposition were 3000 Pa and 620 °C, respectively. The time of synthesis was 25 minutes. The technology of hybrid nanomaterials, step by step, is in our laboratory reproducibly mastered.

- The existence of created hybrid nanomaterials and the quality and nature of carbon deposited on/into the inorganic substrates are confirmed by Raman spectroscopy and electron microscopy.

By the microscopic techniques we observe the morphology of the hybrid nanomaterials, Raman spectroscopy analyse the vibration modes in dependence on the type of the carbon nanotubes. Hybrids evaluated with regard to the presence of carbon phases and metals, and the mechanism of CNTs growth and creation of nanotube grids.

RESULTS AND CONCLUSION

1) We prepared hybrid nanomaterials on natural minerals: montmorillonite, zeolite, pyrophyllite, kaolinite, nontronite, sepiolite, chrysotile, vermiculite and on samples obtained from mining waste from the water flowing out of the mine (see Figs.1. – 9.).
2) We reproducibly verified that the catalytic activity and the formation of CNTs on montmorillonite (MMT) is clearly linked to the presence of iron.
3) We verified the high catalytic activity of Fe-zeolite (natural zeolite, clinoptilolite, impregnated by a solution of ferric chloride) conditioned by the zeolite structure that allows anchoring of Fe^{3+} catalyst particles inside the pores and hereby prevents their migration from the sample.
4) Nanocomposite of Fe-pyrophyllite (natural layered phyllosilicate) was characterized by the formation of aggregates of catalyst particles and consequent formation of bundles of carbon nanotubes. In the case of kaolinite as a carrier substrate, CNTs were located between the crystallinities, grew through the whole volume of substrate and formed 3D grids. In the case of nontronite and sepiolite the CNTs grow through the volume mineral and form a clearly identifiable separated phase. While in the case of nontronite CNTs are disordered, in the case of sepiolite they are aligned in parallel.
5) A unique phenomenon was found with MMT, zeolite and kaolinite. Bridging of iron catalyst particles carbon nanotubes and creation of grids were observed. The distance connected by nanotubes ranged from several nm to 10 micrometers.
6) The results of our work proved that mining waste products contained in waters still leaking form from flooded ore mines can be successfully used for the synthesis of carbon nanotubes and for hybrid nanomaterials formation.
7) Important knowledge was deduced from the qualitative interpretation of the Raman spectrum of CNTs and from electron diffraction. The walls of the nanotubes contain nanocrystalline graphite and the presence of molybdenum was confirmed in the cavities. TEM, EDS and Mössbauer spectroscopy of the terminal parts of the nanotubes revealed the presence of a catalytically active metal.

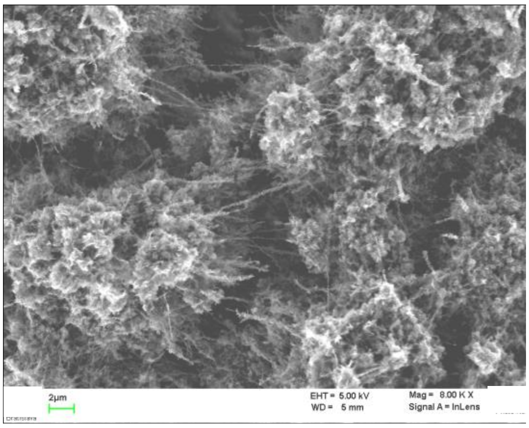


Fig. 1:
SEM image of the CNT bridges grown on Fe-montmorillonite pretreated with $Fe(NO_3)_3 \cdot 9H_2O$

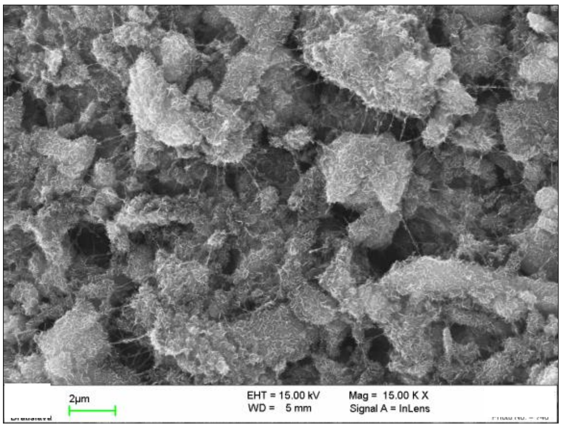


Fig. 2:
SEM image of CNT bridges grown on Fe-zeolite pretreated with $FeCl_3{\cdot}6H_2O$.

Fig. 3:
SEM image of CNTs on sepiolite. The length of CNTs is about 30 micrometers.

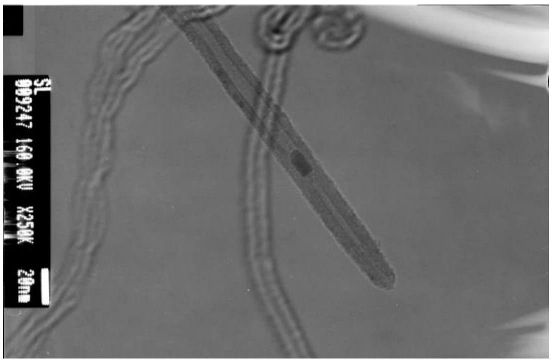
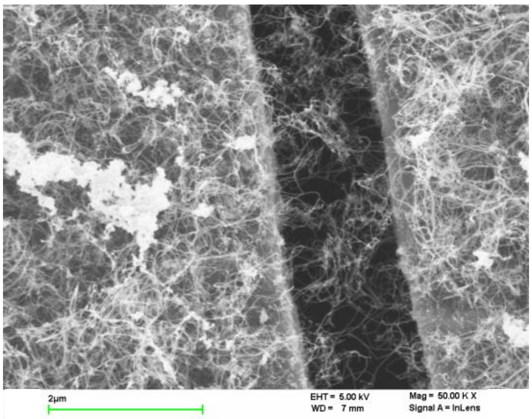


Fig. 4:
TEM image of CNTs on sepiolite. The diameters of carbon nanotubes grown on sepiolite are in the range of 10 nm to 30 nm.



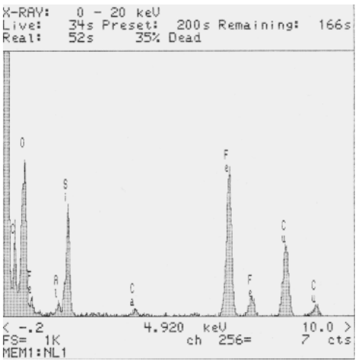


Fig. 5:
SEM image of CNTs on nontronite.
Fe, Al, Si, and Ca are detected by EDS elemental analysis in catalyst particles encapsulated at the tips of CNTs on nontronite.

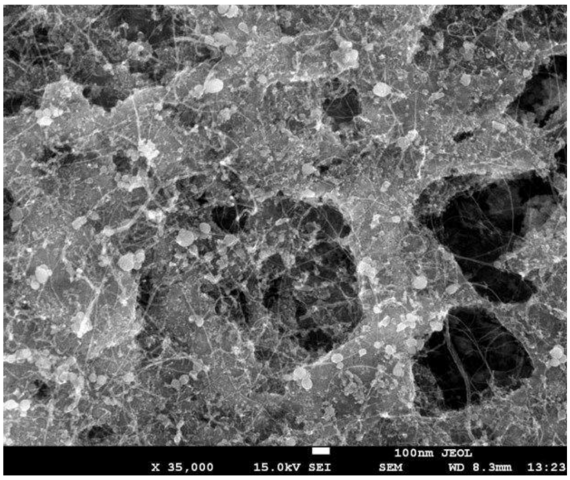


Fig. 6:
SEM image of CNT bridges grown on Fe-vermiculite pretreated with $Fe(NO_3)_3$ $9H_2O$. Nanotubes grown on the surface and in the matrix are interconnected by flakes of mica.

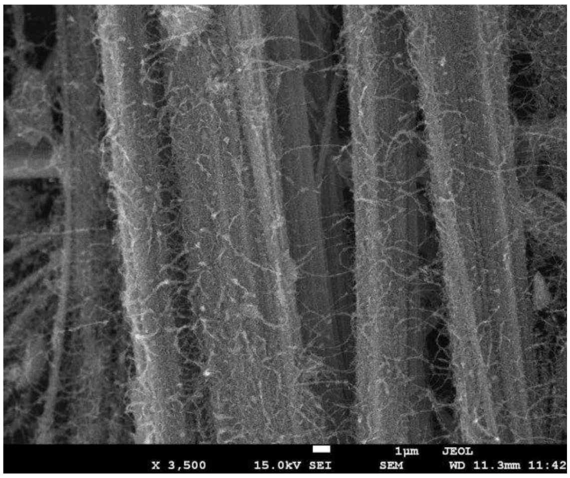


Fig. 7:
SEM images of the fibrous structure of chrysotile after synthesis of CNTs. CNTs create cross-bridges between single fibres.

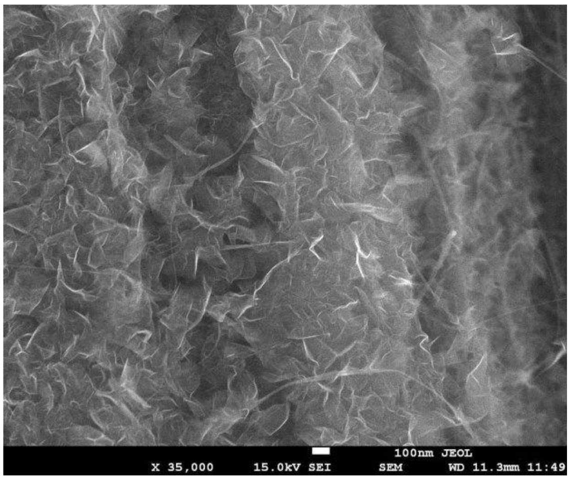


Fig. 8:
The surface of the fibres of chrysotile covered most likely by graphene flakes.

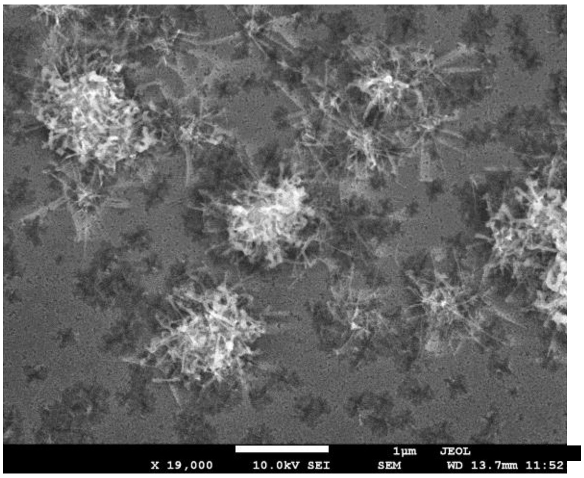


Fig. 9:
SEM micrograph of CNTs synthetized on the clots of mine waters from Smolník (Slovakia). In case the clot agglomerates create islands of catalytic particles, the CNTs have a tendency to cross-bridge single centres.

In our laboratory we have already created hybrid nanomaterials and synthesized carbon nanotubes by CVD on different surfaces (polished, unpolished, conductive, semiconductive, non-conductive, etc). Our published works show that synthesis of CNTs can also be carried out on minerals with a 3D structure. The structure and morphology of the natural inorganic materials are the main advantages utilized in experimental study of the synthesis of their composites with CNTs. Our experimental results confirm the effect of surface morphology and of the matrices of minerals on the distribution of the catalytic particles of iron and at the same time on the morphology of the carbon deposit.

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