

# FORMATION OF NANOCOMPOSITES BASED ON CARBON NANOTUBES AND MONTMORILLONITE, CHRYSOTILE AND VERMICULITE

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## 1. Introduction

Carbon nanotubes (CNTs), thanks to their outstanding properties, have been in the focus of interest of scientists for 25 years [1]. Inorganic composites with carbon nanotubes nowadays constitute new areas of research of fibrous nanomaterials [2-4]. The aim of this paper is to contribute to the understanding of the way of binding and distribution of CNTs in a mineral matrix. In the presented work we follow up our own results in catalytic synthesis of nanocomposites. We prepared nanocomposites based on CNTs and phyllosilicates: synthetic montmorillonite and natural minerals of zeolite, pyrophyllite, kaolinite, nontronite and sepiolite [5-10].

## 2. Experimental materials and conditions

Synthetic montmorillonite (MMT) was prepared by 6 day lasting hydrothermal synthesis in an autoclave (Lampart, Hungary) with a volume of 1 litre at a temperature of 300°C and pressure 8.8 MPa. The starting compounds were aluminium nitrate, magnesium nitrite, ferric nitrite and amorphous silicon dioxide with particles of 5 to 50 nm in size (Aerosil, Evonik Industries, France). The ratios of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO and Fe<sub>2</sub>O<sub>3</sub> in the prepared product were 4:1:0.6:0.1. Synthetic MMT contained 5 wt% of Fe<sub>2</sub>O<sub>3</sub>. Samples were taken from MMT prepared in this way for two experiments: 1) mechanical degradation of synthetic MMT was performed by milling in a common laboratory achate dish, 2) incorporation of iron as a Fe(NO<sub>3</sub>)<sub>3</sub> catalyst was performed from an aqueous solution.

Chrysotile (white asbestos) was isolated from serpentinite from the locality of Dobšiná. Vermiculite for experimental studies was taken from a commercial substrate of expanded vermiculite used for thermoinsulation purposes.

Metal impregnated samples were prepared by sorption from an aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with concentration  $c = 0.1 \text{ mol}\cdot\text{dm}^{-3}$  of silicate. Afterwards, suspensions of the minerals were deposited on a silicon substrate by a micropipette and dried first at room temperature and then in a drier at 110°C.

Synthesis of carbon nanotubes was carried out in the HF CVD reactor. The working atmosphere was a mixture of methane and hydrogen. The precursors are activated by five tungsten filaments heated up to 2200°C. The pressure and temperature during deposition were 3000 Pa and ≈600°C, respectively. The synthesis time was 25 minutes. The quality and nature of carbon deposited on the silicate and the growth of CNTs within the matrix were examined by scanning electron microscopy (JEOL, Japan) and Raman spectroscopy (HORIBA Jobin Yvon, France).

### 3. Results

#### 3.1 *Synthesis of CNTs on mechanically destroyed montmorillonite*

In order to resolve the question as to which extent iron contained in the silicate structure contributes to the formation of CNTs we conducted an experiment on samples of synthetic MMT with a high content of iron incorporated in the structure of MMT.

In our experience, after CNTs synthesis one can roughly identify the presence of the carbon phase also visually because carbon considerably changes the colouring of MMT. Detailed observations, by means of SEM and Raman spectroscopy, of synthetic ferric MMT destroyed by milling confirmed the absence of CNTs and of other amorphous forms of carbon after its exposure in HF CVD (Fig. 1). Denudation of iron, which is part of the basal structure of this clay material, caused by mechanical milling provides no positive result for the synthesis of CNTs. Preliminarily we conclude that the iron atoms contained in the structure of MMT do not exhibit catalytic activity.

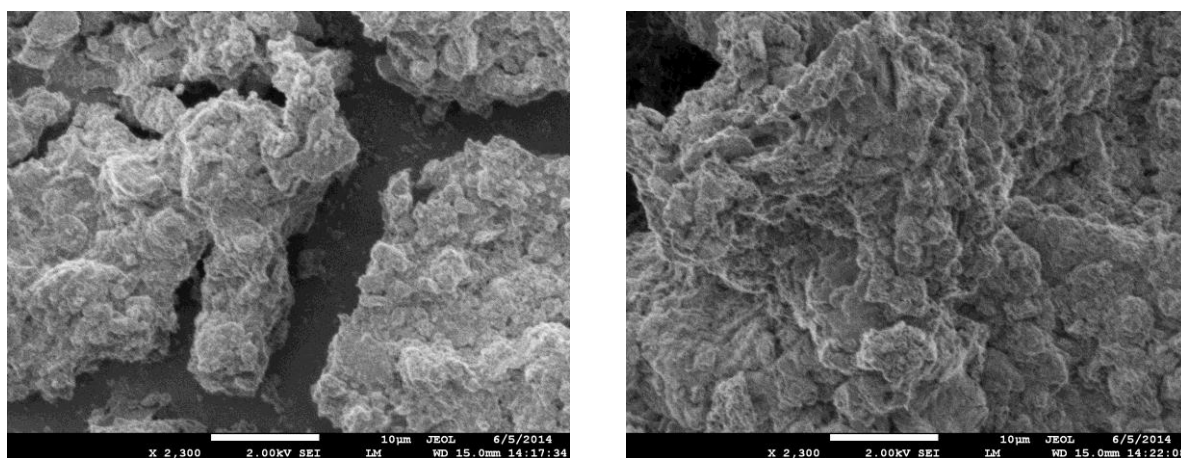


Fig. 1. *SEM images of synthetic ferric MMT destroyed by milling confirm the absence of CNTs after its exposure in HF CVD.*

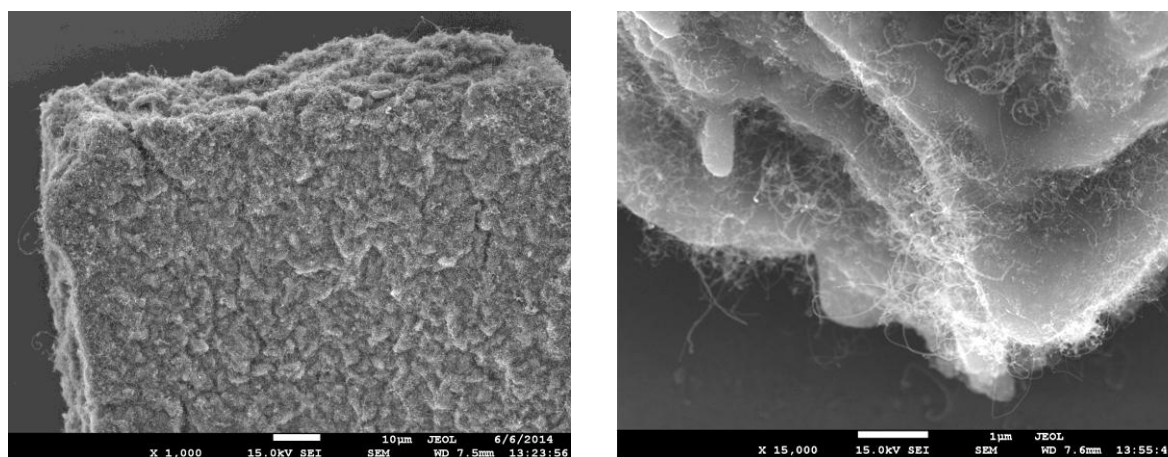


Fig. 2. *SEM images of the layered structure of crystalline MMT after synthesis of CNTs. Left – frontal view of the nanocomposite, right – detail.*

### 3.2 Catalytic synthesis of CNTs on crystalline forms of minerals impregnated by iron

We prepared nanocomposites based on CNTs + synthetic montmorillonite, CNTs + chrysotile and CNTs + vermiculite. Synthesis of CNTs on minerals enriched in iron was successful. Figure 2 shows nanotubes grown on synthetic MMT impregnated by ferric ions (mostly by trivalent atoms Fe(III) [7]). The surfaces of the mineral layers are covered by non-aligned CNTs with various diameters and shapes. The length of single CNTs varies in a wide range, the longest CNTs have lengths from 20 to 30  $\mu\text{m}$ . SEM observations cannot confirm unambiguously that CNTs do not penetrate also the interlayer spaces of MMT. The fibrous structure of chrysotile and the deposited layer of carbon fibres are clearly identified in Fig. 3. The surface of chrysotile fibres is covered also by graphene layers, Fig. 4. Finally, the plate-like structure of vermiculite can be seen in Fig. 5. Microscopic observations of the carbon deposit on chrysotile and vermiculite confirms also formation of grids and cross-bridges between single parts of the surface of the minerals.

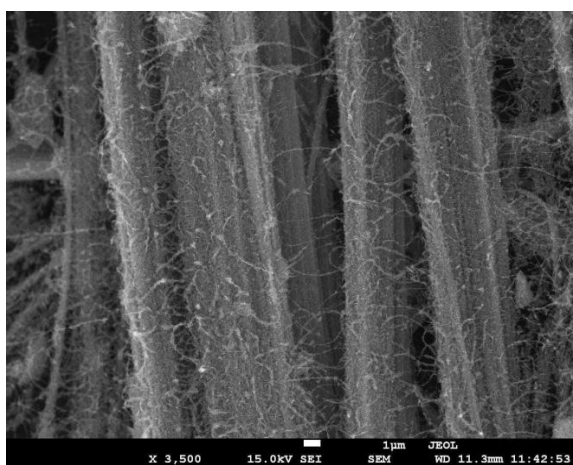


Fig. 3. SEM images of the fibrous structure of chrysotile after synthesis of CNTs. CNTs create cross-bridges between single fibres of chrysotile.

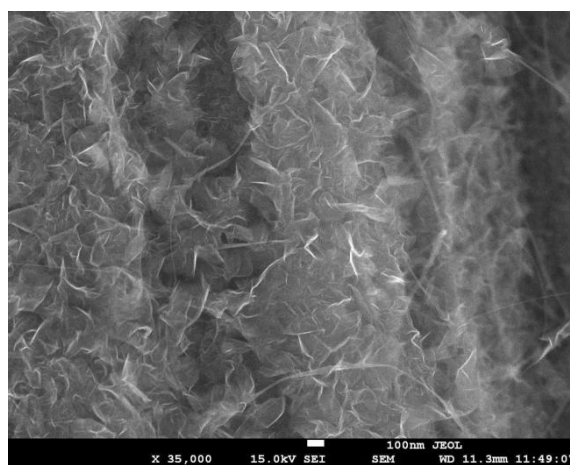


Fig. 4. The surface of the fibres of chrysotile covered most likely by graphene flakes. This fact still has not been confirmed by Raman spectroscopy.

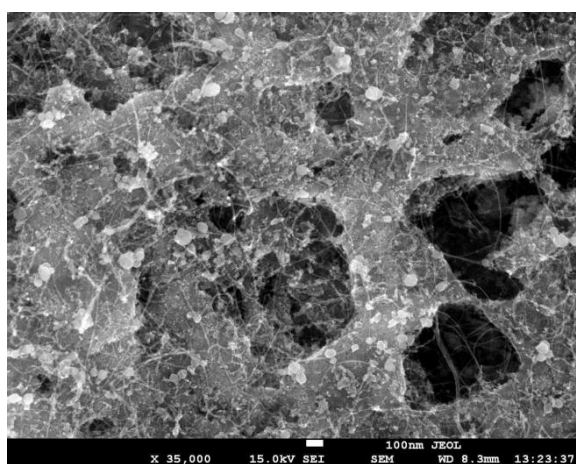


Fig. 5. SEM image of CNT bridges grown on Fe-vermiculite pre-treated with  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ . Nanotubes grown on the surface and in the matrix are interconnected by flakes of mica.

## 4. Conclusion

The structure and morphology of the clays are the main advantages utilized in experimental study of the synthesis of their composites with CNTs. Experimental results confirm the effect of surface morphology and of the matrices of phyllosilicate minerals on the distribution of the catalytic particles of iron and at the same time on the morphology of the carbon deposit.

The most significant result of this study is the discovery that iron atoms which are part of the structure of the clay mineral montmorillonite showed catalytic activity in the synthesis of CNTs neither on the crystalline nor on the amorphous substance obtained by milling of synthetic MMT. The degree of mechanical destruction was verified by X-ray diffraction. The two results imply that synthesis of CNTs on natural forms of MMT can only be achieved by artificial incorporation of a catalytic phase. This result could be expected also for other types of phyllosilicates. MMT has the ability to multiply its volume by water swelling. The existence of negative charge on the stack of MMT has the consequence that the colloidal particles of MMT in aquatic sediments behave as anions with ion exchange properties, thus in an aqueous solution of ferric salts MMT can be enriched with iron ions, hereby providing a matrix containing the  $\text{Fe}^{3+}$  (as well as  $\text{Fe}^{2+}$ ) catalyst for the formation of nanocomposites. Based on our experimental knowledge we conclude that the catalytic activity of the silicates for synthesis of CNTs is not related solely to the ion exchange mechanism.

## Acknowledgement

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