SYNTHESIS OF CARBON NANOTUBES ON COLLOIDAL RESIDUES AFTER ORE MINING AT THE SITES NEAR RUDŇANY AND SMOLNÍK

Magdaléna Kadlečíková[1], Juraj Breza[1], Michal Kolmačka[1], Karol Jesenák[2], Michal Hubeňák[2], Magdaléna Bálintová[3]

[1] Faculty of Electrical Engineering and Information Technology,
Slovak University of Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia
[2] Faculty of Natural Sciences, Comenius University,
Mlynská dolina CH-2, 842 15 Bratislava, Slovakia
[3]Faculty of Civil Engineering, Technical University of Košice,
Vysokoškolská 4, 042 00 Košice, Slovakia

E-mail: juraj.breza@stuba.sk

Received 28 April 2016; accepted 13 May 2016.

1. Introduction

Nanocomposites based on carbon nanotubes (CNTs) may be prepared of substances containing any of the catalytically active metals. One group these substances are artificially prepared materials, the second group are of natural origin. Even though the cleanliness and other important physical and chemical properties of the synthetic compounds may vary in a very wide range, synthetic substances are generally more homogeneous than materials of natural origin. However, there are several reasons for using natural inorganic substrates 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 inorganic materials. This contribution presents the use of fine grained precipitates from mine waters for the synthesis of CNTs. The main components of the colloidal residues resulting from the extraction of ores are microscopic particles containing catalytically active metals.

2. Experimental materials and conditions

Experimental synthesis of CNTs was carbon nanotubes was carried out on samples obtained from mining waste from the shore dark sediment settling ponds in Markušovce and from the water flowing out of the mine in Smolník. The tailing pond between Markušovce and Rudňany was used to collect water after flotation processing of the iron ore.

Copper and iron ores were mined in the local mines between the villages of Smolník and Smolnícka Huta for more than 700 years. They contained mainly minerals chalcopyrite and pyrite. In the late 18th and early 19th centuries also copper and silver ores were mined. At that time, Smolník was the largest mining town in the Spiš region that even competed in importance with Banská Štiavnica. In the twentieth century, the local mines constituted a region with the highest concentration of ore mining in former Czechoslovakia. In the second half of the 20th century, copper, mercury and baryte were retrieved from the ore mined at Markušovce. The main mineral harvested was chalcopyrite for copper production but from 1900 to 1960 pyrite from these mines was processed into sulphuric acid. The mining activity was stopped in 1990. The slow dissolution of sulphide minerals persistently contaminates the stream of Smolník particularly by high concentrations of sulphate anions of arsenic, copper, zinc, manganese and iron.

Mineralogical composition of the dark sediment from the settling pond in Markušovce was described in detail in [1-4]. The main components are siderite $FeCO_3$, quartz SiO_2, baryte $BaSO_4$, muscovite $KAl_2O_{10}(OH,F)_2$ and dolomite $CaMg(CO_3)_2$. Heavy fractions of these wastes contain pyrite FeS_2, chalcopyrite $CuFeS_2$and tetrahedrite $Cu_{12}Sb_4S_{13}$. Composition of the sediment used in this study corresponds mineralogically to the heavy fraction. The sample consisted of particles smaller than 1 μm and in a small extent it also contained agglomerates with a size approaching 10 μm. The sample of the sediment was not treated chemically. It was ground in an agate mortar and applied to a silicon substrate with a size of 1 cm × 1 cm as an aqueous suspension.

The suspension of Smolník tailings contains high concentrations of the typical elements of pyrite waste. These are Fe, As, Cu Zn, Mn as well as elements from silicates that were lye-dipped in nature by acid products such as Al, Mg, Ca, and K [5]. Analyses had shown that one litre of water from the mine site Smolník contains approximately 300 mg of Fe of different oxidation numbers, 4 mg of Cu^{2+}, 9 mg of Zn^{2+}, 26 mg of Mn^{2+}, 73 mg of Al^{3+}, 3200 mg of SO_4^{2-} [6]. A sample of fine grained inorganic precipitate for the synthesis of CNTs was isolated from the mine water with a volume of 800 ml which was precipitated by addition of 1 M aqueous NaOH. Before precipitation, one litre of mine water contained 270 mg of Fe, 1.66 mg of Cu, 7.83 mg of Zn, 22 mg of Mn and 3200 mg of SO_4. Subsequently, 2 ml of an aqueous solution of hydrogen peroxide were added with 31 wt% concentration of H_2O_2. The main component of the dry precipitate was $Fe(OH)SO_4$. The precipitate was ground in an agate bowl. Figure 1 shows a precipitate containing rarely isolated crystalline aggregates.

Afterwards, the aqueous suspensions of the mining waste were deposited on silicon substrates by a micropipette and dried first at room temperature and then in a drier at 110 °C so as to remove water completely.

Synthesis of carbon nanotubes was carried out in the hot filament 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 620 °C, respectively. The time of synthesis 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

Microscopic analysis of the nano-composite synthesized in the HF CVD reactor shows that the sediment from the settling ponds in Markušovce has a high content of particles capable of catalyzing the synthesis of CNTs. The density of CNTs is so high that the sediment they create a continuous carbon layer on the sediment, Fig. 2a. CNTs have a random orientation and

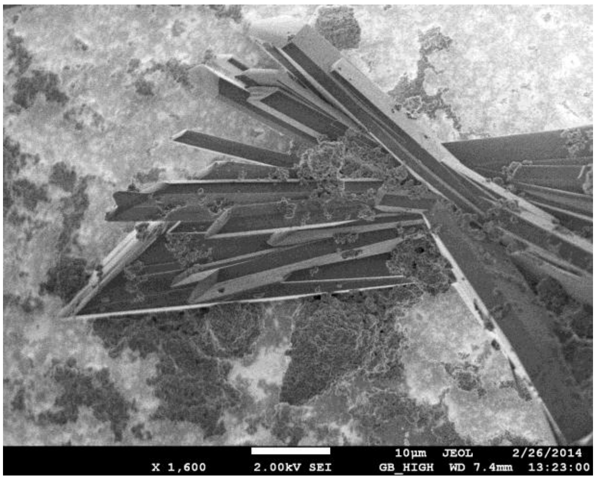
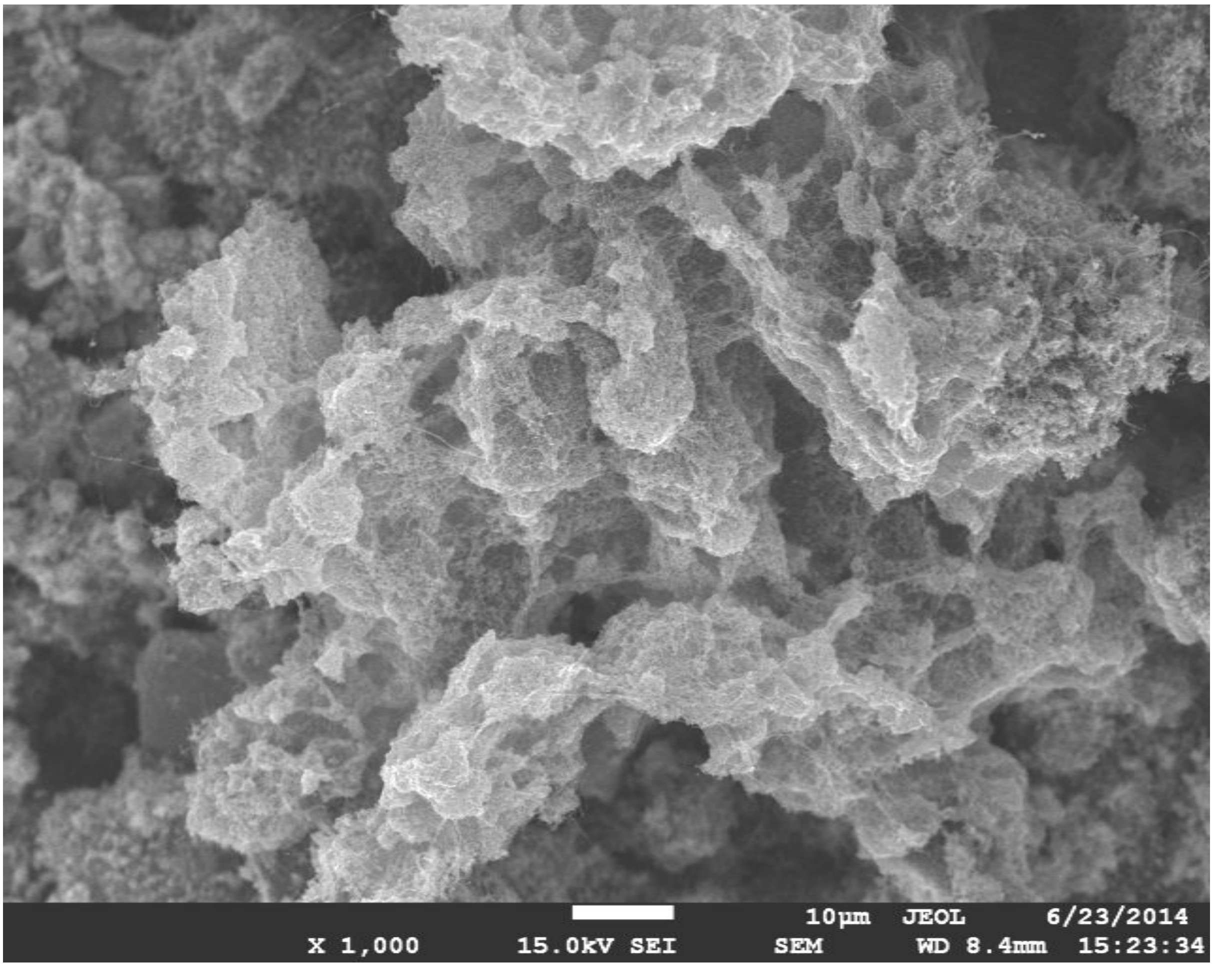


Fig. 1: *Crystalline aggregate found in a sample of mine waste from Smolník. Judging by its appearance, it is probably arsenopyrite. Neither XRD nor chemical analysis of the crystallites was conducted.*

vary in the shape, diameter and length. Their length is several micrometres. The surface of the sediment and the surface of CNTs is coated with graphene flakes, carbon nanowalls (see Fig. 2b) as confirmed by Raman spectroscopy.



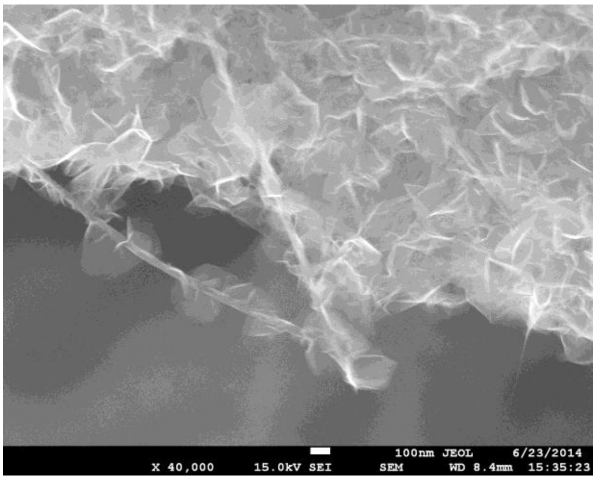


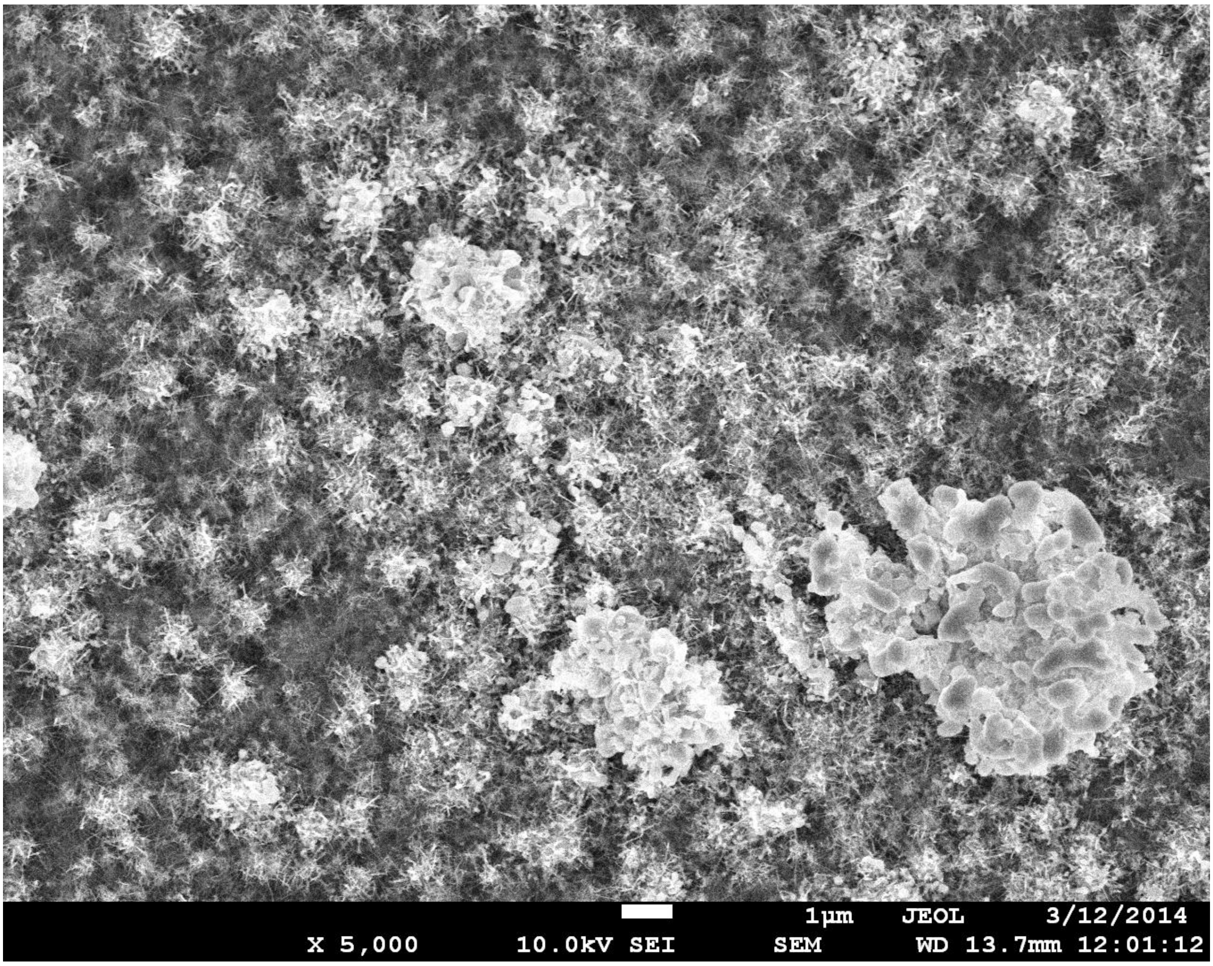
Fig. 2a: *SEM micrograph of the layer of CNTs covering the surface of the sediment from the settling pond in Markušovce.*

Fig. 2b: *Detail of CNTs with a layer of graphene flakes, carbon nanowalls on the sample of the sediment from the settling pond in Markušovce.*

The SEM micrograph of the clot of mine water from Smolník shows two types of particles. The first type are agglomerates of small particles with a size of 0.5 to 1 µm, sporadically more. The second type are beam-like crystals whose size is as big as 40 µm. Judging by their appearance, this is probably arsenopyrite FeAsS.

The SEM micrographs (Figs. 3a and 3b) show the nanocomposite formed during exposure of the mining precipitate to a mixture of hydrogen and methane in the reactor.

Microscopic analysis of the deposits showed that also the precipitate layers from Smolník provide a catalytic substrate for synthesis of CNTs. The density of CNTs in the layer depends on the surface density of the catalytic centres. A layer with a high density CNTs and crosslinking was formed on the areas with a high density of the precipitate from Smolník, see Fig. 3a. In the case of separated catalytic centres the islands of catalyst particles lie at a mutual distance of 100 to 300 nm. The resulting nanocomposite was overgrown and the CNTs have a tendency to bridge the single centres as shown in Fig. 3b.



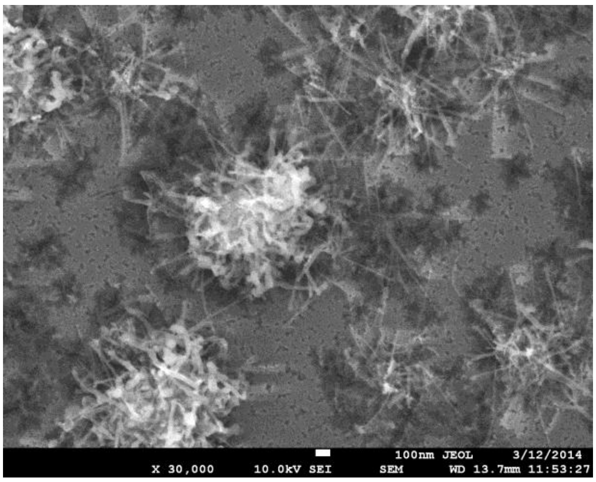


Fig. 3a: *SEM micrograph of CNTs synthesized on the clots of mine waters from Smolník.*

Fig. 3b: *In case the clot agglomerates create islands of catalytic particles, the CNTs have a tendency to cross-bridge single centres.*

4. Conclusion

Research of mine waters attracts considerable attention worldwide because they present a particularly dangerous type of mining waste. These waters mobilize high concentrations of toxic metals. The results of this work prove that mining waste products such as tailing pond sediments and fine iron precipitates contained in waters still leaking form from flooded ore mines can be successfully used for the synthesis of carbon nanotubes and for nanocomposites formation. It was found that the catalytically active species for synthesis of CNTs contained in the sediment from the settling ponds Markušovce are significantly more efficient than those from the precipitates obtained from Smolník mine waters. Nevertheless, our experiments cannot provide firm conclusions about the type and content of catalytically active and inactive particles in mining waters.

Potential industrial use of mining wastes in nanotechnology is based upon the content of catalytically active metals stemming from the initial raw materials. In the case of chemical precipitation, as described in this paper, it would be useful first to address the issue of separation of catalytically active and inactive components of these fine grained precipitates.

Acknowledgement

We are grateful to the scientific grant agency VEGA for financial support of project No. 1/0947/16.

References

[1] M. Petrák, G. Kučerová, R. Tóth, B. Lalinská-Voleková, P. Šottník, Ľ. Jurkovič, E. Hiller, J. Vozár: *Mineralia Slovaca,* **43**, 395 (2011).

[2] E. Hiller, B. Lalinská-Voleková, M. Chovan, Ľ. Jurkovič, T. Klimko, M. Jankulár, R. Hovorič, P. Šottník, R. Fľaková, Z. Ženišová, I. Ondrejková: *Applied Geochemistry,* **27,** 598 (2012)

[3] R. Tóth, E. Hiller, M. Petrák, Ľ. Jurkovič, P. Šottník, J. Vozár, K. Peťková*: Mineralia Slovaca***, 45,** 125 (2013).

[4] E. Hiller, M. Petrák, R. Tóth, B. Lalinská-Voleková, Ľ. Jurkovič, G. Kučerová, A. Radková, P. Šottník, J. Vozár: *Environ. Sci. Pollut. Res*. **20**, 7627 (2013).

[5] O. Lintnerová, K. Mangová, L. Líška, P. Španek: *Mineralia Slovaca*, **43**, 95 (2011).

[6] A. Šlesárová, J. Zeman, M. Kušnierová: IMWA Symposium 2007: Water in Mining Environments, R. Cidu & F. Frau (Eds), 27-31 May 2007, Cagliari, Italy.