CREATION OF NANOCOMPOSITES BASED ON CARBON NANOTUBES AND NANOTUBES OF TiO_2 OR NANORIBBONS OF SODIUM TITANATE

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Abstract

Nanocomposites based on carbon nanotubes and nanotubes of TiO_2 or nanoribbons of sodium titanate were prepared in three technology steps. The source substance in the synthesis of TiO_2 nanotubes was a powder containing nanoparticles of TiO_2. The second source material was a powder of TiO_2 plus sodium hydroxide. These materials were suspensed and subsequently synthesized in a steel autoclave. On the products of hydrothermal synthesis – TiO_2 nanotubes and nanoribbons of sodium titanate – a catalytic layer was deposited by repeated sorption from a water solution of $Fe(NO_3)_3$. Onto inorganic matrices prepared in this way, synthesis of carbon nanotubes was carried out at 600°C using a methane/hydrogen mixture during hot filament chemical vapour deposition. The quality and nature of the nanocomposite were examined by electron microscopy and Raman spectroscopy. We studied the growth mechanisms of carbon nanotubes and the influence of the type and shape of the inorganic matrix upon the morphology of the final nanocomposite.

Keywords: Nanocomposites, carbon nanotubes

1. INTRODUCTION

One of the most significant research routes of carbon nanotubes (CNTs) is directed on the creation of their composites with inorganic matrices of different structures and with catalytically active metals. Since the family of catalytically active metals for CNTs synthesis can nowadays be considered closed, the main topic is the influence of the physical and chemical properties of inorganic matrices upon the morphology and properties of the carbon phase. Such features as the shape, length and diameter of CNTs and mutual orientation of singe CNTs are of foremost interest. Following up with our previous studies of the growth of CNTs on minerals [1, 2] we pointed at the differences in building the nanocomposites. Suitability of other materials for the synthesis of nanocomposites based on CNTs is examined. The contribution presents the studies of the deposit of CNTs on samples of TiO_2 nanotubes and nanoribbons of sodium titanate that contained catalytically active iron. The experiment was designed to answer the question if sorption of Fe^{3+} ions from a solution of ferric nitrate leads to their preferential cumulation on the edges and terminal surfaces of inorganic matrices and to reveal the morphology of nanocomposites based on carbon nanotubes and nanotubes of TiO_2 or nanoribbons of sodium titanate.

2. EXPERIMENTAL MATERIALS AND METHODS

Nanocomposites based on carbon nanotubes, nanotubes of TiO_2 and nanoribbons of sodium titanate were prepared by three technology steps. Preparation procedure of TiO_2 nanotubes and of sodium titanate nanoribbons was derived from the procedure reported in [3]. The source substance in the synthesis of TiO_2 nanotubes was a powder containing nanoparticles of TiO_2 (Degussa Aeroxide® TiO_2 P 25). The second source material was a powder of TiO_2 plus sodium hydroxide (Lachema Brno) and a water solution of NaOH, c(NaOH)=11.25 mol.dm^{-3}. Hydrothermal synthesis of the two substances was performed in teflon vessels in a steel autoclave. The main product of 24 hour synthesis are nanotubes, the main product of 48 hour synthesis were nanoribbons. A catalytic layer was deposited on the TiO_2 nanotubes and sodium titanate nanoribbons by repeated sorption from a water solution of $Fe(NO_3)_3$ with concentration c=0.1 mol.dm^{-3}. In situ creation of nanocomposites and synthesis of carbon nanotubes was performed by hot filament chemical vapour deposition in an HF CVD reactor. The precursors were activated by five tungsten filaments heated up to 2200°C. The working atmosphere was a mixture of methane and hydrogen. The pressure and temperature during deposition were 3000 Pa and approx. 600°C, respectively. The quality and morphology of the matrix and of the carbon deposited onto the inorganic matrices were examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy.

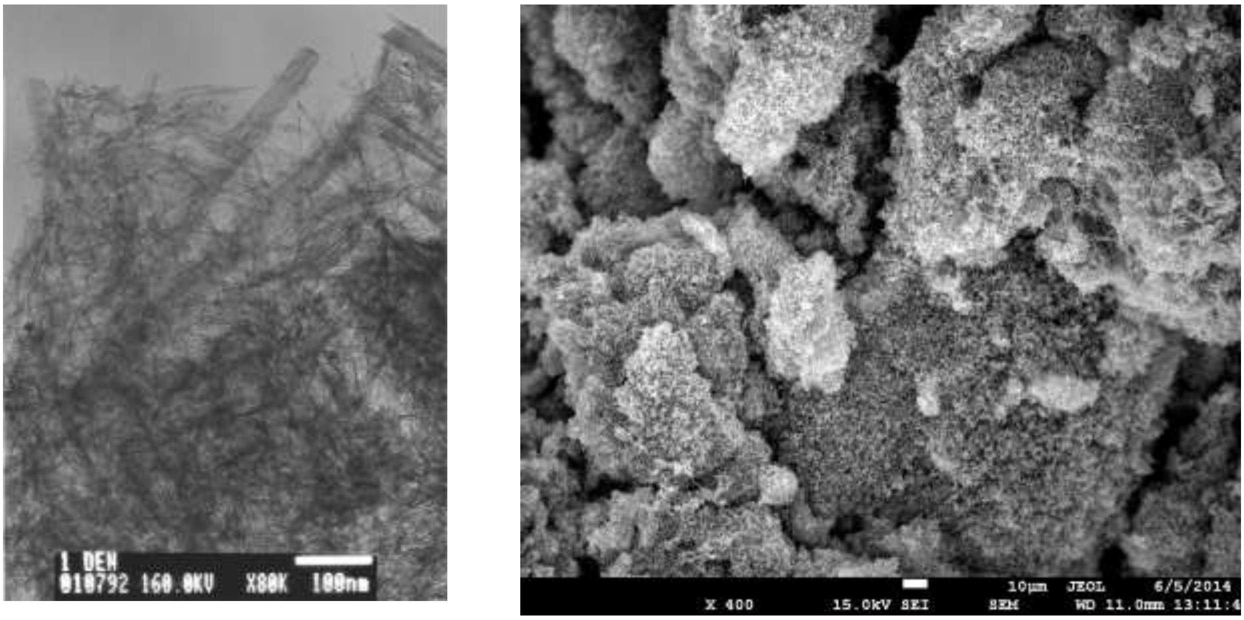

Fig. 1 TEM of nanotubes of TiO_2 made by the hydrothermal method (left), and SEM of the nano-composite based on carbon nanotubes and nanotubes of TiO_2.

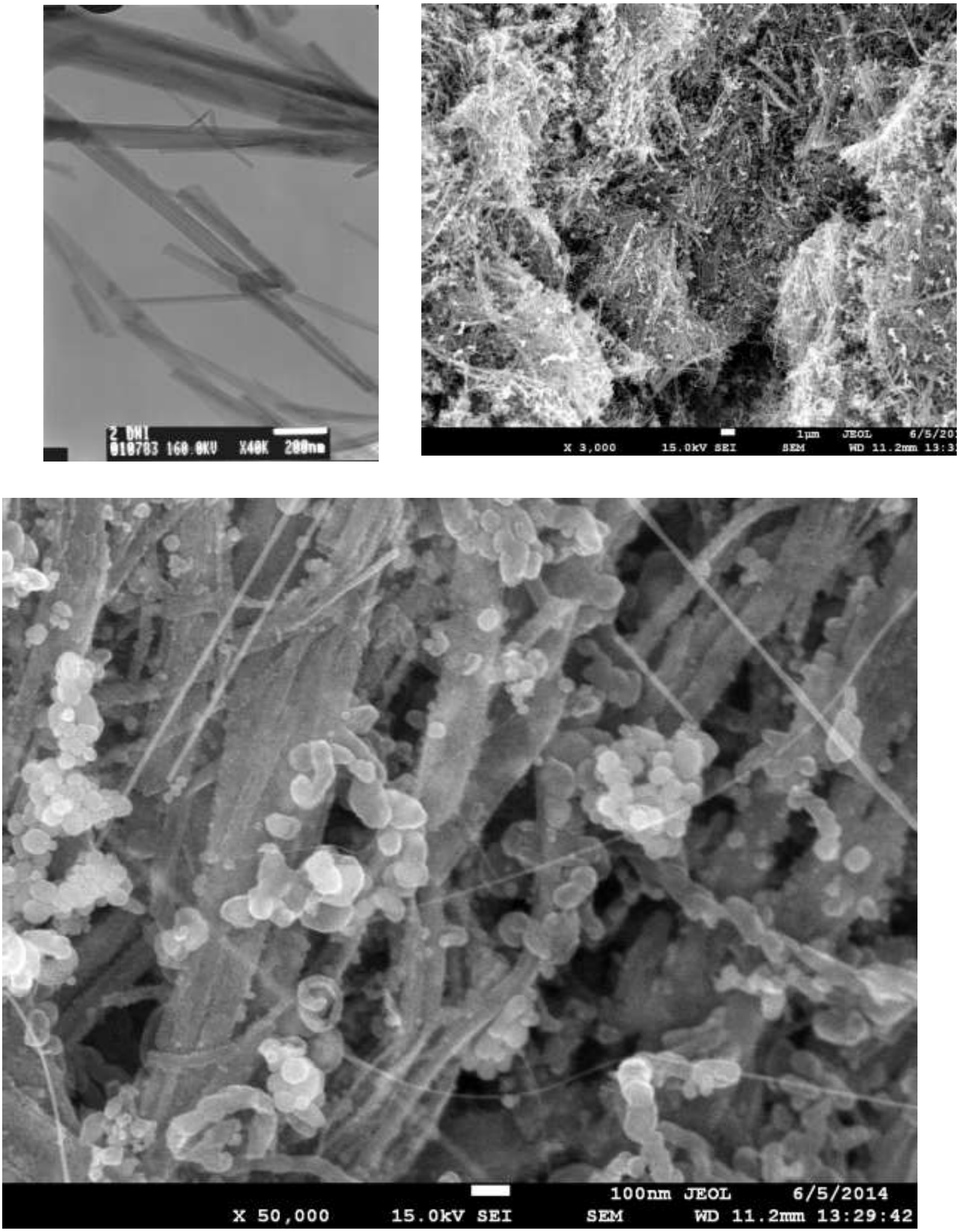

Fig. 2 TEM of nanoribbons of sodium titanate made by the hydrothermal method (top left), SEM of the nanocomposite based on carbon nanotubes and nanoribbons of sodium titanate (top right), and detail of the nanocomposite in which the nanoribbons, salt and CNTs are recognizable (bottom).

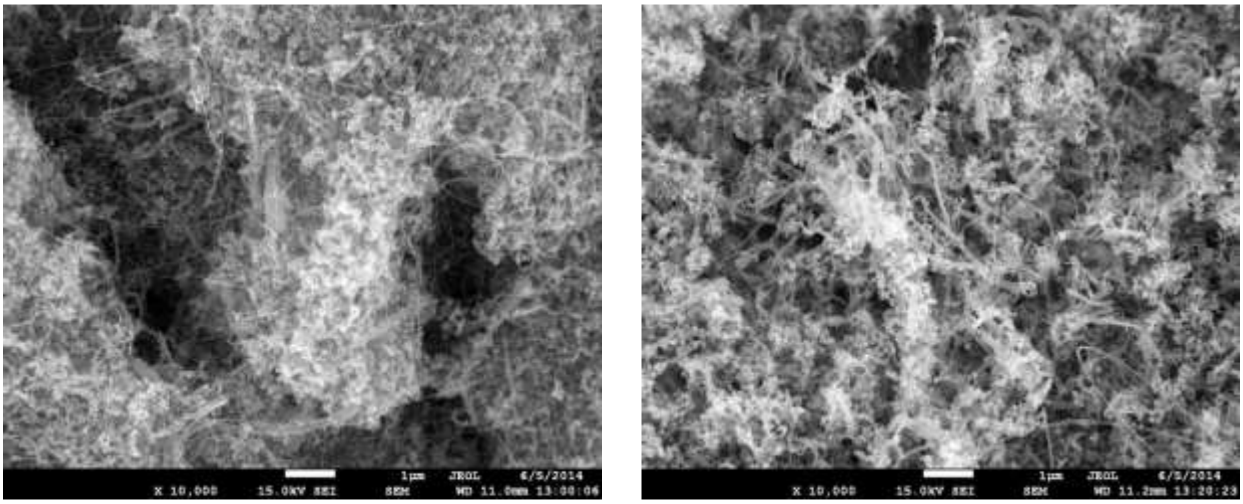

Fig. 3 Distribution of the catalytic particles of ferric salt (white dots) in the matrices of TiO_2 nanotubes (left) and of the sodium titanate nanoribbons (right).

3. RESULTS AND DISCUSSION

The main components of hydrothermal synthesis were identifies by TEM, see Figs. 1 (left) and 2 (top left). Both types of inorganic matrices – TiO_2 nanotubes and sodium titanate nanoribbons – contained also other particles with dimensions from 20 to 100 nm. The subsequent process of the sorption of catalytic ferric salt particles was efficient ion both matrices, as shown in Fig. 3. No preferential cumulation of Fe^{3+} ions on the edges and surfaces of the inorganic matrices from the solution of ferric nitrate was observed. Morphological studies confirm that both of the matrices are grown through by carbon nanotubes. The carbon deposits on the two types of samples were mixtures single-walled, multiple-walled carbon nanotubes (SWCNTs and MWCNTs) and amorphous carbon. As for their shape and diameter, CNTs creates a non-uniform phase containing carbon nanotubes with a length from several hundreds nanometres up to tens of micrometers and with variable orientation.

Even though the distribution of catalytic particles on the two types of inorganic matrices was not different markedly, the final products of CNT synthesis on the two inorganic matrices were not identical, see Figs. 1 (right) and 2 (top right). Expected twining of carbon nanotubes on the templates of nanotubes or nanoribbons was not observed. An older SEM micrograph explains the expected morphology of the nanocomposite based on carbon nanotubes and nanotubes of TiO_2 or nanoribbons of sodium titanate.

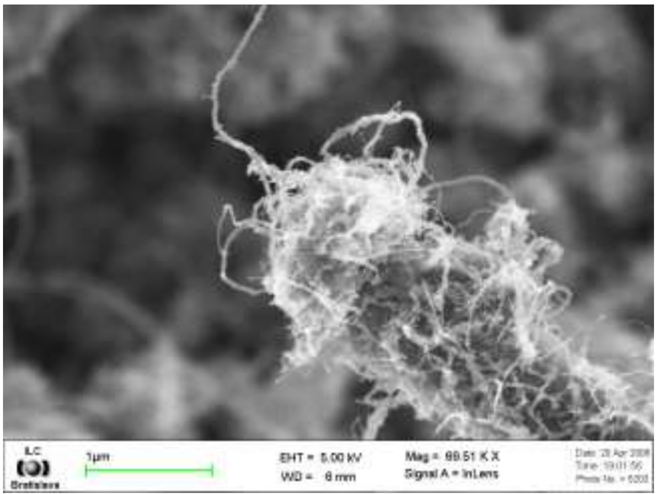

Fig. 4 Twining of carbon nanotubes on the templates

4. CONCLUSIONS

The fundamental idea to prepare one-dimensional materials and their nanocomposites with CNT assumes that fibrous nanocomposites based on nanotubes and titanates will have unique properties for practical applications such as energy conversion and storage and as photocatalyst for the environmental remediation [4, 5]. The hydrothermal method was employed to transform spherical TiO_2 nanoparticles and to synthesize TiO_2 nanotubes and nanoribbons of sodium titanate, and subsequently to fabricate nanocomposites based on CNTs by HF CVD. In the two inorganic matrices, no specific cumulation of the particles of ferric salt was observed on the edges and surface. Catalytic efficacy of the ferric salt eventually manifested itself in the amount, density and distribution of carbon nanotubes, in their shape, diameter and orientation. It was found that the morphology of the resulting nanocomposite depended neither on the cumulation of ferric salt particles nor on the defining shape of the matrix components. Both matrices are grown through by CNTs, thus a fibrous nanocomposite was fabricated successfully. Its morphology is different than it was expected: twining of carbon nanotubes on the templates of nanotubes or nanoribbons was not observed. Most likely, this result was not affected by the presence of impurities.

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