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COMPOSITES THEORY AND PRACTICE

Iryna M. Ivanenko*, Tetiana A. Dontsova, Igor M. Astrelin
Vladislav V. Kuzmenko

National Technical University of Ukraine «KPI», Department of Chemistry
4 Bld., 37 Prospect Peremogy, Kyiv 03056, Ukraine
** Corresponding author: E-mail: irinaivanenko@hotmail.com*

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SYNTHESIS OF TIN(IV) OXIDE - CARBON NANOTUBES NANOCOMPOSITES BY SOL-GEL METHOD

Tin(IV) oxide - carbon nanotube nanocomposites were synthesized by the sol-gel method without and with ultrasonication, microwave radiation, and cavitation. The synthesized products were examined by means of transmission electron microscopy (TEM), X-ray diffraction, and differential thermal analysis methods. The TEM micrographs have shown that the tin (IV) oxide was deposited onto the oxidized surface of MWCNTs. The X-ray diffraction patterns have shown that the crystallite size of the SnO_2 was within the 6.7÷11 nm range. The thermal analysis data indicate that the thermal stability of the SnO_2 - MWCNTs composites increases versus the initial carbon nanotubes. The scheme of transformations in the tin(IV) oxide - carbon nanotube nanocomposite synthesis by the sol-gel method was proposed.

Keywords: sol-gel method, tin(IV) oxide, MWCNT, nanocomposite, ultrasonication

SYNTEZA NANOKOMPOZYTÓW TLENEK CYNY(IV) - NANORURKI WĘGLOWE METODĄ SOL-GEL

Nanokompozyty tlenek cyny(IV) - nanorurki węglowe wytworzono metodą sol-gel bez oraz z użyciem ultradźwięków, promieniowania mikrofalowego oraz kawitacji. Produkty syntezy badano metodami transmisyjnej mikroskopii elektronowej (TEM), dyfrakcji promieniami X oraz różniczkowej analizy termicznej. Mikrogramy TEM ujawniły osadzanie się tlenku cyny(IV) na utlenionej powierzchni MWCNTs. Otrzymane dyfraktogramy rentgenowskie pozwoliły na określenie wielkości krystalitów SnO_2 w zakresie 6.7÷11 nm. Uzyskane z analizy termicznej wyniki wskazują na wzrost stabilności termicznej kompozytów SnO_2 - MWCNTs w porównaniu z początkowymi włóknami węglowymi. Zaproponowano schemat przemian w nanokompozytach tlenek cyny(IV) - nanorurki węglowe wytworzonych metodą sol-gel.

Słowa kluczowe: metoda sol-gel, tlenek cyny(IV), MWCNT, nanokompozyty, ultradźwięki

INTRODUCTION

Tin oxides are applied successfully as sensitive materials in gas sensors and biosensors, catalysts for fuel cell electrodes, materials of Li-ion batteries, ultracapacitors etc. [1-5]. Nanocrystalline tin(IV) oxide exhibits the best characteristics in comparison to the macrodispersed form. However, due to its low stability, SnO_2 nanoparticles can be obtained only on the well-developed surface of common carbon matrices (activated carbon, graphite etc.) or advanced carbon nanomaterials like carbon nanotubes. Metal oxide - carbon nanotube nanocomposites can be obtained by various methods such as chemical deposition, hydrothermal synthesis, the sol-gel process, etc.

Among various chemical synthesis methods for the preparation of metal oxides with small-sized particles, the sol-gel process offers several advantages over other methods, including its simple procedure, better homogeneity, etc. For better homogeneity, morphology, crystallite size and distribution, metal oxides on the carbon nanotubes surface can be influenced by additional processing like ultrasonication, cavitation, and microwave radiation. However, the effect of such treatments in the nanocomposites synthesis process on the size, morphology and distribution of tin(IV) oxide nanoparticles on the carbon nanotubes surface has not been not been studied extensively.

This paper presents the practical synthesis of the tin (IV) oxide - carbon nanotube nanocomposite by the sol-gel method with and without additional treatment as well as investigation of the obtained material properties.

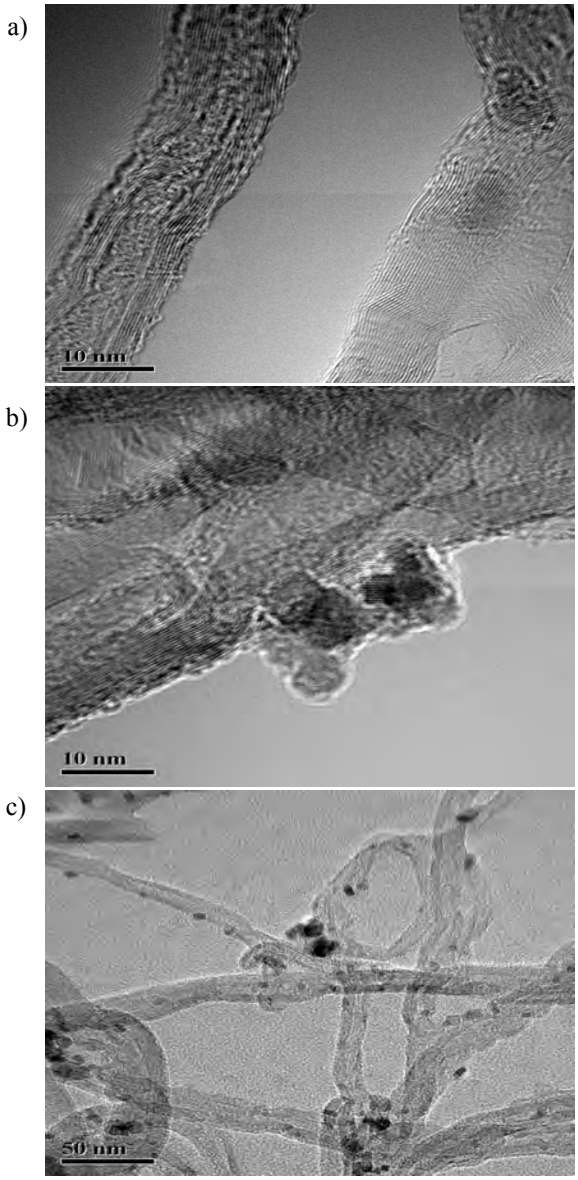

Fig. 1. TEM images of initial carbon nanotubes (a) and of tin(IV) oxide – MWCNTs nanocomposite (b and c)

Rys.1. Obrazy TEM nanokompozytu tlenek cyny(IV) - nanorurki węglowe

MATERIALS AND EXPERIMENTAL PROCEDURE

Multiwalled carbon nanotubes (MWCNTs) were synthesized by thermal chemical vapor deposition (CVD) from a mixture of propylene and hydrogen at the $Mo/Fe/Al_2O_3$ catalyst surface. The outer diameter of individual nanotubes was 15÷30 nm, and the inner one was 5÷8 nm (Fig. 1a). The specific surface area of the MWCNTs determined by the desorption nitrogen method was 130 m^2/g.

The MWCNTs were purified from the remnants of the catalyst to a purity degree of no less than 96 mass %. The as-prepared MWCNTs were at first treated by refluxing in nitric acid (40%) during 2 hours to improve their dispersity in aqueous solutions by forming oxygen-containing functional groups on their side walls [6-8]. The surface functional composition of the initial and oxidized MWCNTs was investigated by the Boehm method (Table 1).

TABLE 1. **Content of surface oxygen-containing groups on MWCNTs before and after oxidation**

TABELA 1. **Zawartość powierzchniowa grup zawierających tlen na MWCNTs przed i po utlenianiu**

Samples	Functional groups content [mmol/g]		
	Phenolic	Carboxylic	Lactonic
Initial MWCNTs	0,4	0	0
Oxidized MWCNTs	1,1	0,3	0

Samples of the nanocomposite were obtained by the chemical sol-gel method as follows. $SnCl_2 \cdot 2H_2O$ (2.5 g) was dissolved in a 50 mL isopropanol solution, intensively stirred with a magnetic stirrer during 2 hours, and allowed to age during 24 hours. Then the 0.5 g acid treated MWCNTs were added to the aged solution and the resulting suspension was separated into four parts: the first was left unchanged (Sample 1), the second was ultrasonicated (Sample 2), the third was irradiated by microwaves (Sample 3), and the fourth was treated with cavitation (Sample 4). All the treatments were carried out for 10 minutes. After evaporation of the solvent, each precipitate was annealed at 500°C for 2 hours in an electric furnace. Ultrasonification was carried out using an ultrasonic homogenizer (УЗДН-2Т, Ukraine, 44 kHz, 400 W), radiation was performed in a microwave (Samsung M1712NP, 800 W) and cavitation treatment - using an ultrasound cavitator (ЛУЗД, Russia, 21.7 kHz).

RESULTS AND DISCUSSION

The synthesized samples of the SnO_2 - MWCNT nanocomposite were examined by means of transmission electron microscopy (TEM), X-ray diffraction, and differential thermal analysis.

The images of the SnO_2 in the synthesized samples were obtained by transmission electron microscopy using Leo Supra 50 VP6 equipment with 5 kV voltage (Fig. 1b). The TEM-images have shown that the tin (IV) oxide was deposited on the oxidized surface of MWCNTs in an arbitrary manner as spherical or almost spherical particles with a size of about 7÷15 nm.

According to the JCPDS standard (card No 41-1445), all the samples (Fig. 2) contain only one phase of tin (IV) oxide. The tin(IV) oxide is characterized by a tetragonal rutile structure [9].

Using diffraction data, the crystal grain sizes for all the samples were calculated. The crystal grain sizes of the SnO_2 in the samples were calculated using Debye-Sherer's formula as follows:

$$t = \frac{0.9 \cdot \lambda}{B \cdot \cos\theta} \quad (1)$$

where λ is the wavelength of the X-ray, nm; B is the full width at half the height of the peaks; θ is Bragg's angle.

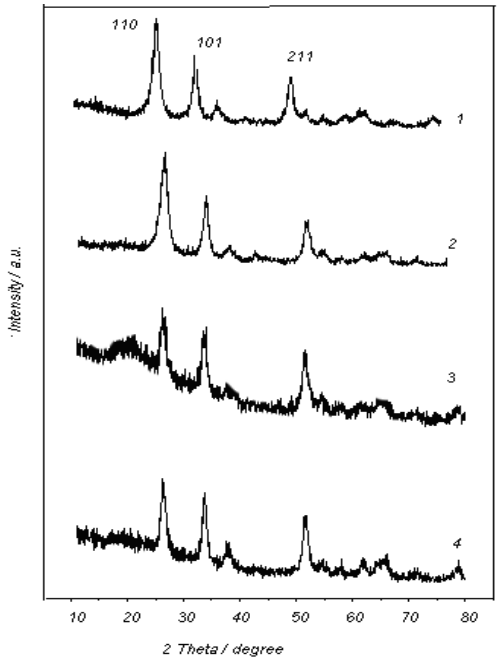

Fig. 2. XRD pattern of synthesized samples: 1 - sample 1, 2 - sample 2, 3 - sample 3, 4 - sample 4

Rys. 2. Dyfrakcja XRD próbek po syntezie: 1 - próbka 1, 2 - próbka 2, 3 - próbka 3, 4 - próbka 4

The width at half the height of the diffraction peaks was calculated using Warren's formula.

The sizes of the tin(IV) oxide crystallites are in the range of 6.7÷11.0 nm (Table 2). Thus, all the synthesized samples have a nanometer size. This is also confirmed by the electron microscopy of these samples (Fig. 1) and corresponds to known literature data [10, 11].

TABLE 2. **Crystal grain sizes of SnO_2 in nanocomposite samples**

TABELA 2. **Rozmiar krystalitów SnO_2 w próbkach nanokompozytowych**

Samples	2θ, deg.	B [rad.]	Crystal grain size [nm]
Sample 1	26.6127	0.026065	7.2
Sample 2	26.6427	0.028719	6.7
Sample 3	26.3541	0.018595	9.2
Sample 4	26.3935	0.015882	11.0

The smallest crystallite size was found in the sample obtained using ultrasonication, and the largest - using cavitation. Moreover, additional treatment during nanocomposite synthesis by the sol-gel method, e.g. microwave treatment after cavitation application, leads to obtaining larger particles of SnO_2 compared to those samples obtained without additional treatment.

An amorphous phase is present in the sample obtained using microwave treatment (Sample 3). None of the other samples do contain the amorphous phase. Thus, we can conclude that only ultrasonication has a positive effect in this system. Sample 2 has the smallest and best-crystallized particles.

Differential thermal analysis was carried out using a simultaneous thermal analyzer Derivatograf Q-1500 with a heating rate of 10ºC/min from 0 to 1000ºC in air atmosphere. According to the thermal analysis data, the initial nanotubes are burned almost completely at the temperature 580÷590°C.

The mass content of the nanotubes in the obtained nanocomposites does not exceed 10.5% (Fig. 3).

The greatest mass loss (10.5%) was detected in Sample 3. Microwave treatment of the suspensions during synthesis results in maximal binding of the carbon nanotubes. Cavitation and the absence of additional treatment lead to an almost identical mass loss (6.5÷6.8%). It can be concluded that in general the treatment with cavitation is inexpedient.

Sample 2 shows the highest content of inorganic components. In this sample, the mass loss is the lowest (3.8%). It can be concluded that under the influence of ultrasound, the largest amount of tin oxide is precipitated on the surface of MWCNTs.

Moreover, comparing two figures (Fig. 3a and 3b), it can be found that the original carbon nanotubes are burned at a temperature of 590°C almost completely (Fig. 3a). The nanotubes in the composites are oxidized by the oxygen in the air and eliminated at a higher temperature, about 640°C (Fig. 3b). It means that an increase in thermal stability of the carbon nanotubes is achieved by binding with tin(IV) oxide.

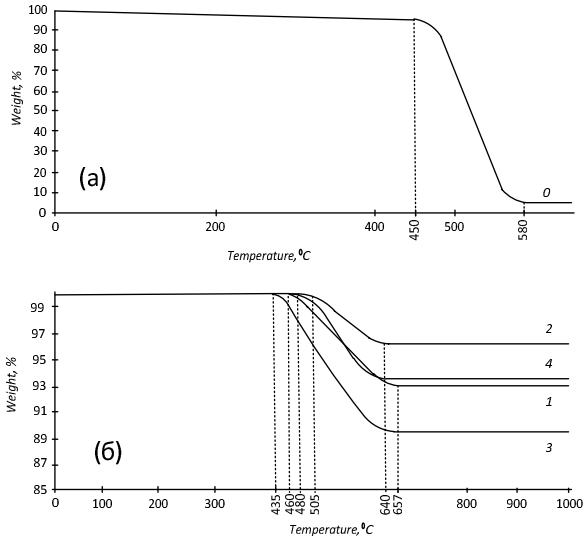

Fig. 3. TG curves of washed initial MWCNTs (a) and synthesized nanocomposites SnO_2 - MWCNTs (b) measured in O_2 atmosphere (mass loss 0 - 95 mass%, 1 - 6.8 mass%, 2 - 3.8 mass%, 3 - 10.5 mass%, 4 - 6,5 mass%)

Rys. 3. Krzywe TG płukanych wstępnie MWCNTs (a) oraz wytworzonych nanokompozytów SnO_2 - MWCNTs (b) mierzone w atmosferze O_2 (strata masy 0 - 95% mas., 1 - 6.8% mas., 2 - 3.8% mas., 3 - 10.5% mas., 4 - 6,5% mas.)

The following is known from the various classic tutorials of inorganic chemistry. The hydrolysis of $SnCl_2$

proceeds with the formation of the intermediate salt $Sn_4(OH)_6Cl$ in the solution and alcohol acts as homogenization agent and promotes the hydrolysis of tin(II) chloride. Gel aging and structuring occurs at standing by the polycondensation of α-tin acid in air at the evaporation temperature. The evaporation of solvents (isopropanol and water) leads to the dehydration of tin hydroxide and the formation of SnO. The process of tin(II) oxide changing to tin (IV) oxide takes place on the stage of calcination in air at a temperature of 500°C:

$$2SnO+O_2\ SnO_2 \xrightarrow{t} 2SnO_2$$

Therefore, if we unite all these fragmentary data from different sources, can get the total sequence of transformations as follows:

$$SnCl_2{\cdot}2H_2O \longrightarrow Sn_4(OH)_6Cl \longrightarrow Sn(OH)_2 \longrightarrow$$
$$5SnO{\cdot}2H_2O \longrightarrow SnO \longrightarrow SnO_2$$

The oxidized carbon nanotubes were added to the solution at the stage of polycondensation of α-tin acid. The carboxylic and phenolic groups on the surface of the oxidized MWCNTs dissociate and exchange their protons for $SnOH^+$ ions present in the solution. Further heating of the obtained suspension leads to the formation and lasting strengthening of the SnO nanoparticles, which transformed into SnO_2 directly on the surface of the nanotubes upon further calcination.

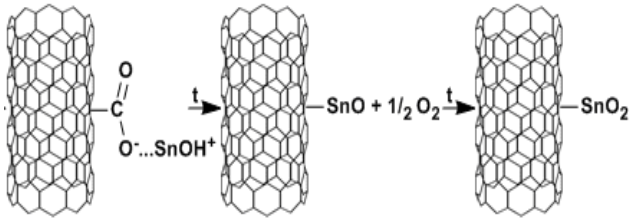

Fig. 4. Formation of tin(IV) oxide - carbon nanotube nanocomposite

Rys. 4. Tworzenie nanokompozytów tlenek cyny(IV) - nanorurki węglowe

SUMMARY

Tin(IV) oxide - carbon nanocomposites were successfully synthesized from carbon nanotubes by the sol-gel method using ultrasonication, microwave irradiation, and cavitation. The TEM images have shown that the tin oxide was deposited on the oxidized surface of the MWCNTs in an arbitrary manner as spherical or almost spherical particles with a size of about 7÷15 nm. Ultrasonic, microwave, and cavitation treatment facilitated the nanocomposite synthesis to different degrees.

The results of the X-ray diffraction investigations have shown that the size of the SnO_2 crystallites is within the range of 6.7÷11 nm. Additional treatment of the suspension by ultrasound allows one to obtain smaller sizes of tin(IV) oxide crystallites, a higher degree of nanoparticles crystallinity, and a lower content of MWCNTs in the nanocomposite. It indicates the positive effect of ultrasonic treatment usage in the sol-gel method of obtaining nanoparticles. The thermal analysis data indicate that the thermal stability for the composites SnO_2 - MWCNTs increases as compared to initial carbon nanotubes.

The proposed scheme of transformations of the synthesis of tin(IV) oxide - carbon nanotubes nanocomposite by the sol-gel method include: SnO_2 nanoparticle nucleation, maturation and aging of SnO sol on the MWCNTs surface, and conversion of tin(II) oxide to tin(IV) oxide, that are all mandatory stages in all the presented modifications of the sol-gel method. These nanoparticles are attached to the surface of oxidized MWCNTs in place of carboxyl and phenolic groups.

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