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Obtaining of composite material based on carbon nanowalls and micro- and nanoparticles

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ABSTRACT

This article is dedicated to the production of composite materials based on carbon nanowalls (CNWs) and micro- and nanoparticles of metal oxides, which today can be used as materials for supercapacitor electrodes due to their high specific surface, mechanical and electrochemical wear resistance. Synthesis of CNWs on the surface of alumina and titanium oxide particles was carried out by chemical vapor deposition in the plasma of a radio-frequency (RF) capacitive discharge of a mixture of argon and methane gases. The obtained samples were examined by using a Quanta 3D (SEM, FEI, USA) scanning electron microscope and NThegra Spectra Raman spectroscope. After PECVD synthesis on aluminum and titanium oxides, the microscopic and spectroscopic analysis of the samples showed different results.

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1. Introduction

Today one of the global challenges in the world is to obtain energy in large quantities and its storage. There are two ways of energy storage electrostatic (capacitor) and electrochemical (batteries). Both of them has own area of application. But recently, so-called "supercapacitors" fall between traditional electrolytic capacitors and rechargeable batteries in lifespan, energy storage, and efficient operating temperature [1–4]. However, supercapacitors often have low energy storage density due to the low specific capacitance of currently available electrode materials. For this reason, the choice of suitable electrode material is one of the keys to obtaining supercapacitors with good characteristics [3].

One of the most promising nanostructured materials for creating supercapacitor electrode is carbon nanowalls (CNWs). CNWs is a two-dimensional (2D) material, which can be described as wall-like carbon nanosheets with several tens of nanometers in thickness, arranged vertically on a substrate [5]. Their high value of a specific surface area, high mechanical and chemical stability, high electrical conductivity and a large number of graphite edges have led to the fact that these materials are used in several applications, such as catalyst substrates, hydrogen adsorption and biological sensors [6–8]. Moreover, due to such excellent properties, CNWs are used as one of the components of a nanostructured composite material in supercapacitor electrode fabrication [9,10]. For example, the authors in [9] obtained an electrode based on CNWs and ruthenium oxide (RuO_2), which shows a specific capacity of more than 1000 mF/cm^2. The work [10] presents the results of obtaining wear-resistant composite material based on CNWs and manganese oxide (MnO_2) with parameters of energy density of 118 Wh/kg, power density of 783 W/kg and preservation of capacity of 92% after a long 2000 charge and discharge cycles at 3 mA/cm^2. There are a lot of works, where micro- and nanoparticles of transition metal oxides (RuO_2, MnO_2, NiO, TiO_2, and WO_3) [11–12] and various carbon nanostructures [13] were widely used, which also represent an excellent characteristic for supercapacitors. In this work, the synthesis of composite materials based on CNWs and micro- and nanoparticles of metal oxides (Al_2O_3 and TiO_2) is considered, which can also be used as nanostructured composite materials for creating electrodes of supercapacitors.

2. Experiments

Synthesis of CNWs was carried out on the surface of micro- and nanoparticles of metal oxides (Al_2O_3 and TiO_2) by chemical vapor

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deposition in an argon (Ar) and methane (CH_4) plasma medium of a radio-frequency (RF) capacitive discharge. The experimental setup and its detail description are given in [14–16]. In our experiment, a box-shaped copper cell with the particles into it was located on the surface of the lower grounded electrode, below which a heating element was fixed. The CNWs synthesis process consists of two stages. At the first stage, for the purity of the experiment and the disposal of various gas impurities inside the working chamber, a vacuum (10^{-5} Torr) is created. Then, an inert Ar gas is introduced into the working chamber at a constant flow of 7 sccm, wherein the gas pressure increased to the value of 1.5 Torr. After turning on the heating element the temperature in the system increases up to the 500 °C and then the plasma of radio-frequency capacitive discharge is ignited between the two electrodes at a power of 10 W. In this case, a plasma etching of the oxide layer on the surface of particles takes place. Plasma etching plays an important role in the formation process of CNWs since in the growth mechanism, Ar ions irradiation is involved [17–19] in the formation of nanoislands and dangling bonds on a growing surface, which leads to the formation of nucleation centers. In addition, Ar ions irradiation enhances the surface reaction in the growth phase, including the adsorption of hydrocarbon radicals

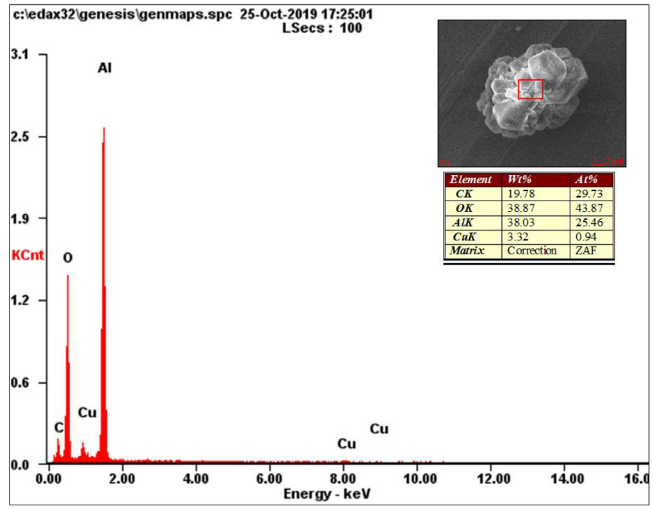

Fig. 3. Analysis of the chemical composition aluminum oxide after the synthesis by the PECVD.

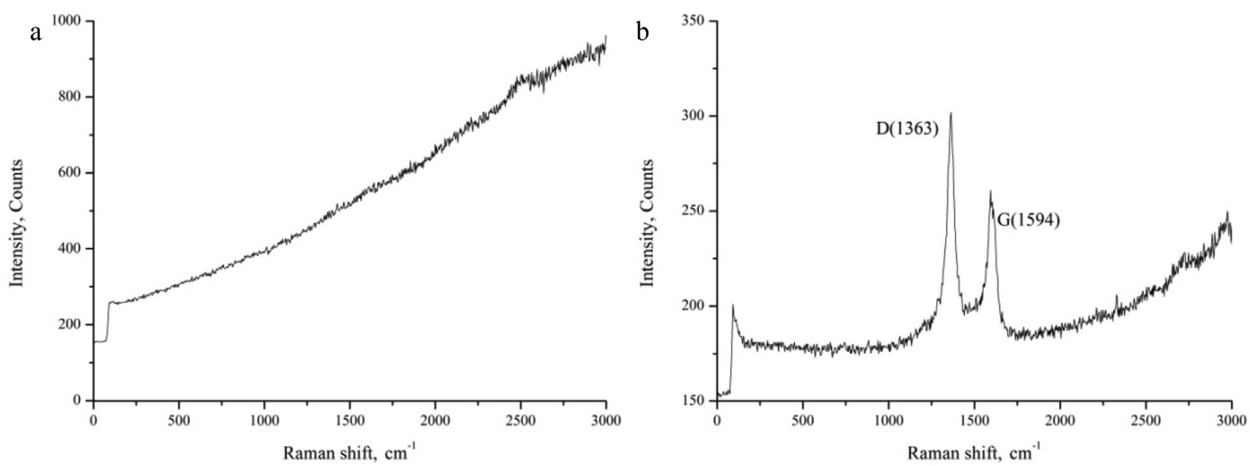

Fig. 1. Raman spectra of alumina oxide micro particles (a) before and (b) after the CNWs synthesis process.

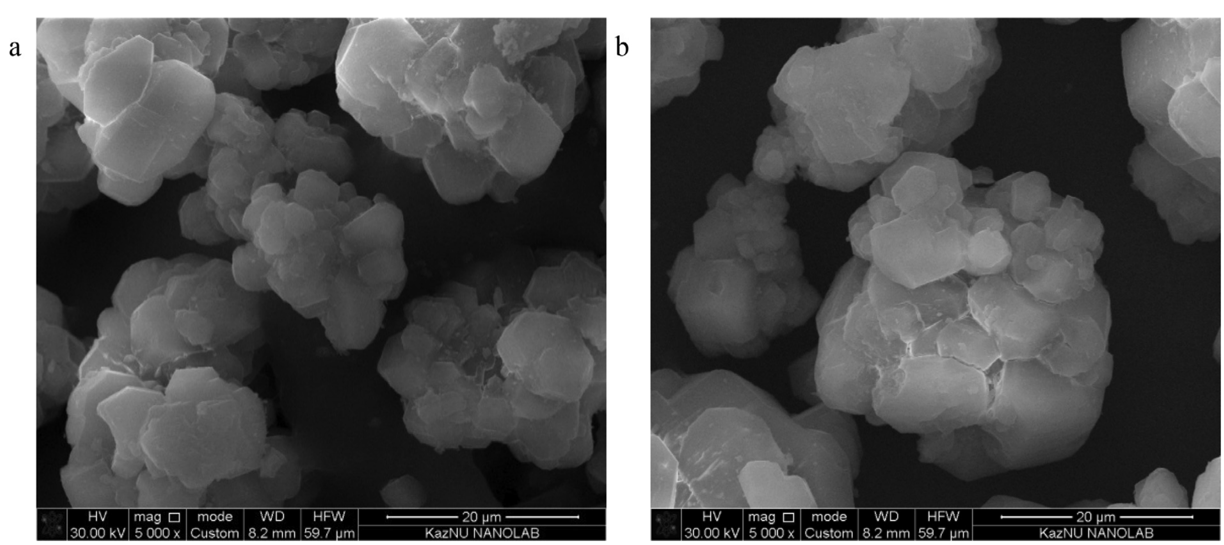

Fig. 2. SEM images of aluminum oxide microparticles (a) before and (b) after the synthesis of CNWs.

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at nucleation sites, while the increase in ion irradiation (higher RF power) prevents the growth of carbon nanowalls due to etching effects. At the next stage of the experiment, carbon-containing gas (CH_4) is introduced into the working chamber with a flow rate of 0.7 sccm, wherein the gas pressure rises to 1.8 Torr. The second stage takes 25 min of time. Thus, the formation of vertical carbon nanowalls on the nucleation centers of the surface of micro- and nanoparticles of metal oxides (Al_2O_3 and TiO_2) takes place. The obtained samples were examined by using a Quanta 3D (SEM, FEI, USA) scanning electron microscope and NThegra Spectra Raman spectroscope.

3. Results and discussion

Figs. 1 and 2 present the results of Raman spectroscopy and scanning electron microscopy analysis of obtained alumina samples after PECVD synthesis. As it's seen, the Raman spectrum of

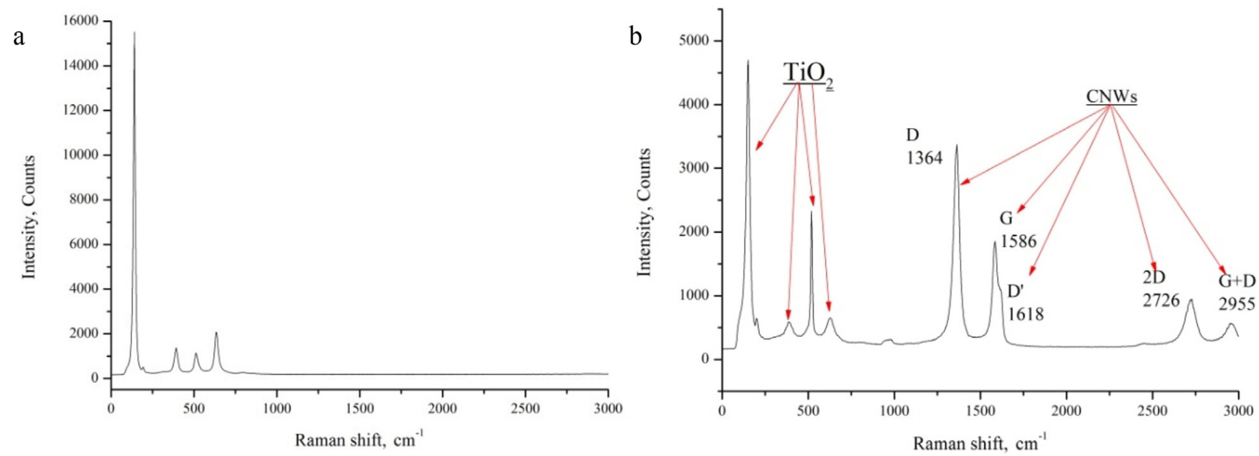

Fig. 4. Raman spectra of nanoparticles of titanium oxide (a) before and (b) after the synthesis of CNWs.

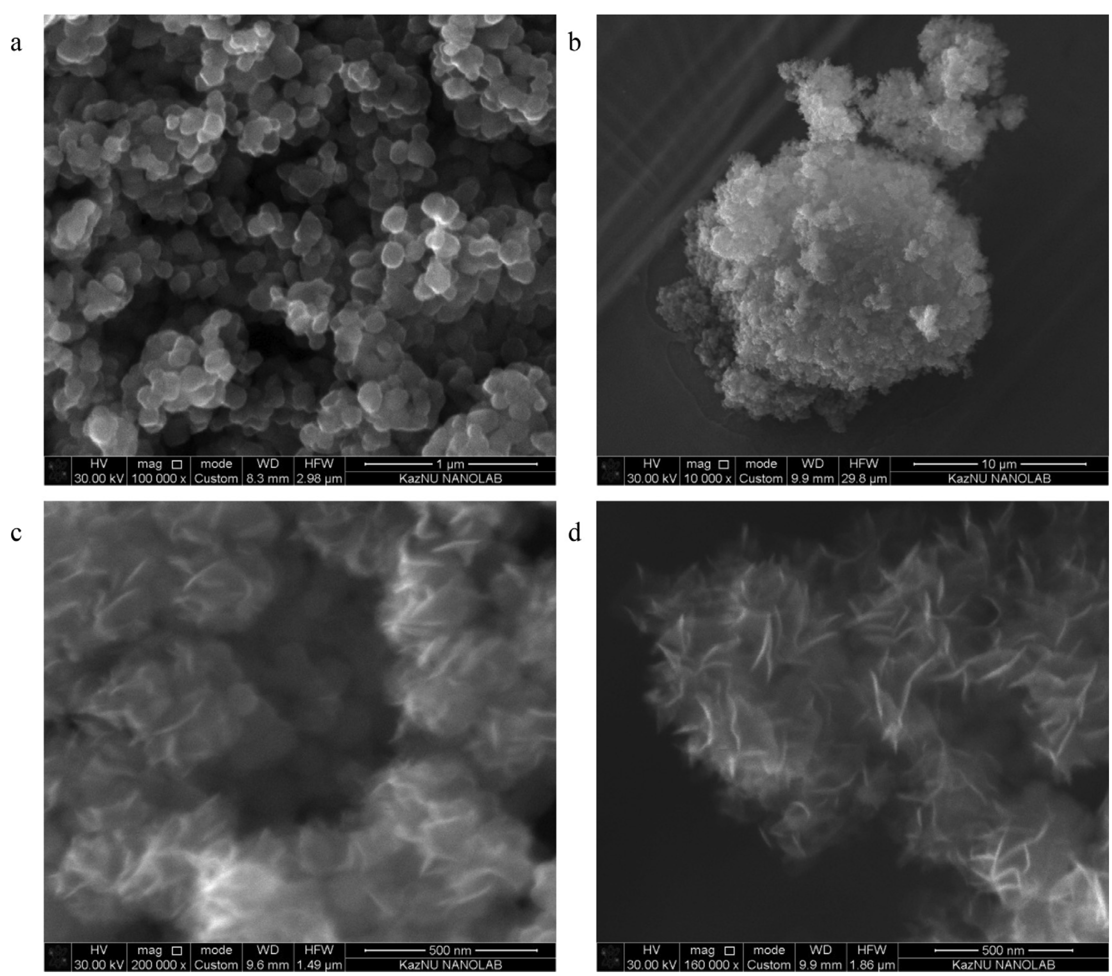

Fig.5. SEM images of titanium oxide nanoparticles (a) before and (b–d) after the synthesis of CNWs.

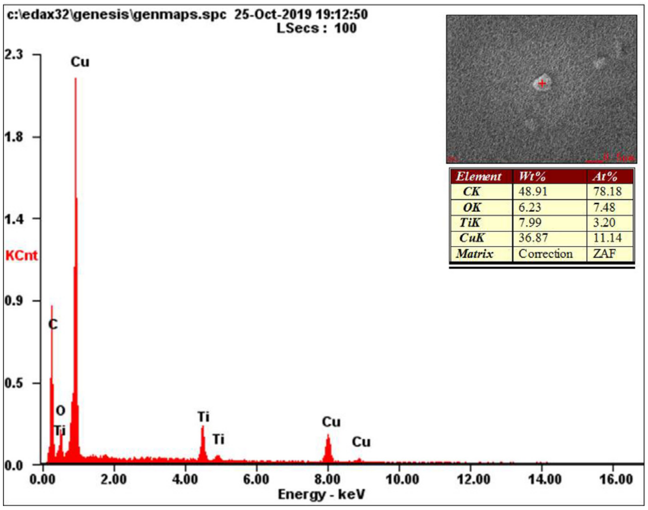

Fig. 6. Analysis of the chemical composition titanium oxide after the synthesis by the PECVD.

the initial alumina oxide particles (Fig. 1a) luminesces, which is typical for this material. After the synthesis process, D (1363) peak, a fissile G peak (1594) and a 2D peak with luminescent are appeared in the Raman spectrum (Fig. 1b). This spectrum can indicate some presence of carbon nanostructures or the most likely carbon amorphous structure in the composite powder of Al_2O_3.

Further, SEM analysis indicates the absence of walls form on the surface of aluminum oxide microparticles, and there are no significant changes in the morphology of alumina before and after the synthesis process (Fig. 2a and b) can be observed. Fig. 3 presents the chemical composition analysis of alumina particles obtained after PECVD synthesis, it is seen that the percentage of carbon in the composition of alumina is too small. The possible explanation of the small percentage of carbon is a thick oxide layer and weak plasma etching, which weaken hydrocarbon radicals' adsorption and the formation of nucleation sites.

A synthesis of CNWs on the surface of titanium oxide nanoparticles (TiO_2) was also carried out. Fig. 4a and b present the results of Raman spectroscopy analysis. The Raman spectrum of the original sample is fully consistent with the spectrum of titanium dioxide with anatase crystal lattice. After the synthesis of CNWs on the surface of titanium oxide nanoparticles, changes in the Raman spectrum can be observed, in addition to the typical peaks of titanium oxide, peaks that completely characterize the CNWs appear. In particular, the peaks, D (1364), G (1586), 2D (2726) and G + D (2955) describe graphitized carbon nanostructure, whereas D'(1618) peak indicates a strong defect structure, which appears due to the free bonds of vertically oriented graphene edges. The presence of CNWs on the surface of titanium oxide nanoparticles is also shown by SEM analysis before and after the synthesis process (Fig. 5). The chemical composition also guarantees the presence of a carbon structure in the resulting material (Fig. 6).

4. Conclusion

In this work, a CNWs synthesis was carried out on the surface of aluminium oxide microparticles and titanium oxide nanoparticles by chemical vapor deposition in radio-frequency capacitive discharge plasma. After CNWs synthesis process on microparticles of aluminum oxide, a certain carbon deposition and most likely carbon amorphous was indicated by Raman spectrum, whereas SEM analysis indicates the absence of CNWs on the surface of the particles. The possible explanation is a thick oxide layer and weak Ar ions irradiation, which weaken hydrocarbon radicals' adsorption and the formation of nucleation sites. Synthesis of CNWs on the surface of titanium oxide nanoparticles was carried out in the same condition as in case of alumina powder. After analysis of obtained samples, Raman spectrum and SEM images show strong deposition of CNWs on the surface of titanium oxide nanoparticles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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