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Structural Studies of C–Ni–Pd Nanocomposite Films Deposited on Al_2O_3 Substrate

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The properties of nanocomposite carbon–nickel–palladium (C–Ni–Pd) films deposited on Al_2O_3 substrate have been investigated and the results are presented in this work. C–Ni–Pd films were obtained by a 3 step process consisting of PVD/CVD/PVD methods. The structure and morphology of the obtained films were characterized by scanning electron microscopy and transmission electron microscopy techniques at various stages of film formation. Energy dispersive X-ray spectrometer was used for measuring the elements segregation in the obtained film. Transmission electron microscopy and scanning transmission electron microscopy observations have shown carbon nanotubes decorated with palladium nanoparticles in the final film. The average size of the palladium nanoparticles did not exceed 10 nm.

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1. Introduction

The sensing properties of carbonaceous–palladium film are widely known. Many groups are working on preparation of hydrogen sensor based on such material. The challenge is low cost of fully reversible, sensitive and working at high temperature and humidity sensor.

Hydrogen gas is an important ingredient in many fields of research and industry, such as fuel cells, automobile engines, chemical production and industrial processing [1]. But, if hydrogen concentrations in air exceeds 4%, then this mixture is easily flammable and highly explosive [2]. Therefore, a sensor that can detect hydrogen gas is strongly required. Various types of hydrogen sensors have been developed based on monitoring changes in electrical [3], optical [4], electrochemical [5], and mechanical [6] signals when the sensors were exposed to hydrogen environment. Fabrication of the sensors for the room temperature detection and monitoring of hydrogen gas is a key to the development of a novel hydrogen-based technology.

Hydrogen sensors based on Pd-dispersed single-walled nanotubes (SWNTs) show good reversible response [7, 8].

Many attempts have been made to develop new biotechnologies to improve the sensitivity and selectivity for gene analysis [9–11] and biosensor design, such as optical [12–16] and electrochemical transducers [17–21]. Due to their special sizes, nanomaterials display novel physical and chemical properties, such as the nanoscale effect and the surface effect. Additionally, nanomaterials open the possibility of miniaturization of the sensing devices into nanoscale, which is important in biological researches. The palladium nanoparticles are employed to electrode modification and design [22]. Zhang et al. showed that nanostructured Pd films modified microelectrodes had shown to be excellent amperometric O_2 sensors in a wide range of O_2 concentrations [23]. Attributed to the unusual properties, carbon nanotubes (CNTs) are the promising carbonaceous materials [24], there has been growing interest in using CNTs in fabricating biological devices owing to their ability to promote the electron transfer in biomolecules [25].

Taking into account the actual state of art for gaseous, bio- and optoelectronic sensor we prepared three components senor based on CNTs, Ni and Pd nanograins. This type of films may be used as a potential sensor of gases (e.g. H_2, NH_3, CO_2) and bio- sensors or optical sensors [26–29]. In our previous papers we have shown that such films can be applied as sensors of some compounds [30–32]. In this paper a new method of C–Ni–Pd thin film preparation for application as a resistive or optical sensor of gases (e.g. H_2, NH_3, CO_2) and biosensors (e.g. glucosamine) is presented.

2. Experimental procedure

Examination films were deposited on Al_2O_3 substrate because of good adhesion to such substrate. Due to the multistep mode of final film forming, substrates having a smooth surface such as silicon or glass have failed.

In the first step the nanocomposite C–Ni film was obtained by evaporation in dynamic vacuum (10^{-4} Pa) from two separated sources containing fullerenes C_{60} (first source) and nickel acetate (second source) (Fig. 1a).

In the second step of process the above film was modified by pyrolysis chemical vapor deposition (CVD) process in which xylene was decomposed in quartz tube reactor at the temperature of 650 °C (Fig. 1b).

Then, in the third step of final film production, on the surface of the C–Ni film, palladium–fullerene films were deposited using physical vapor deposition (PVD) process

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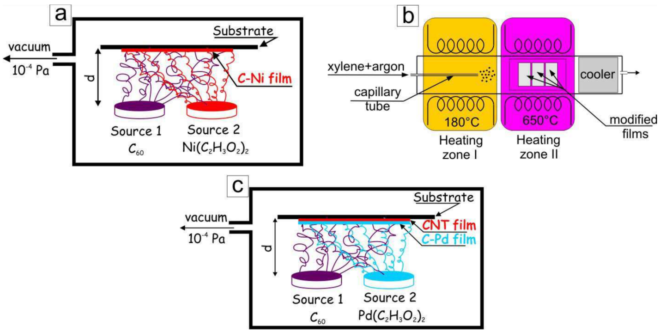

Fig. 1. Schematic presentation of technological process steps: (a,c) PVD setup, (b) CVD setup.

(Fig. 1c). Carbon nanotubes found for these films were covered with palladium nanograins and carbon (Fig. 2).

Scanning electron microscopy (SEM) method was used to examine the morphology of the film at various stages of the film formation. These investigations were performed with the JEOL JSM-7600F field emission scanning electron microscope operating with 5 keV incident electron beam energy.

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) methods were applied to study details of the structure of Pd nanoparticles. These investigations were performed with the Titan 80-300 Cubed high resolution TEM operating at 300 keV incident electron beam energy, equipped with energy dispersed X-ray spectrometer (EDX).

3. Results

The film obtained after first step production was smooth and reflected the topography of the substrate (Fig. 2a and b). A thin film of Ni–C covered the surface of the substrate Al_2O_3. In Fig. 2a grains of ceramic substrate are shown. Ni nanoparticles are invisible in SEM observations because of the very small size. It was only TEM study that has shown that Ni nanograins are visible and were placed in the carbonaceous matrix in these films (Fig. 2c). Ni particle size is in the range of 8–10 nm.

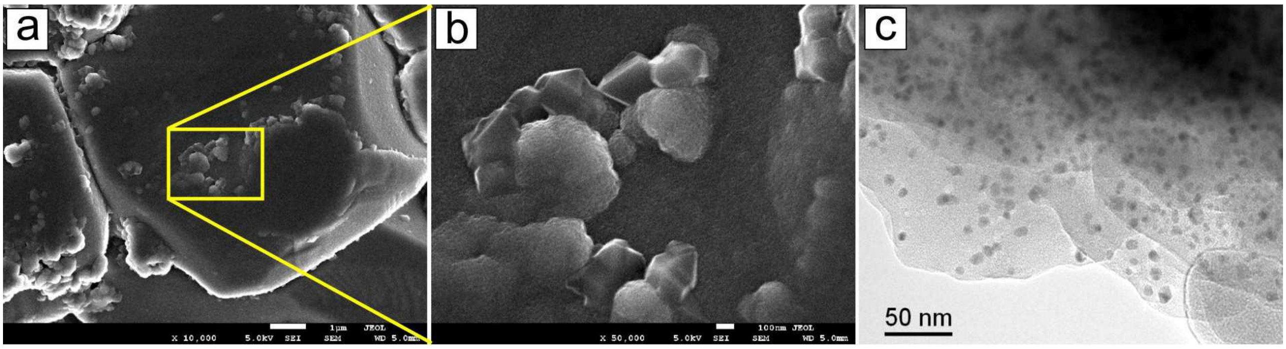

Fig. 2. SEM micrographs of C–Ni film surface (a,b) and TEM micrographs of Ni nanograins (c).

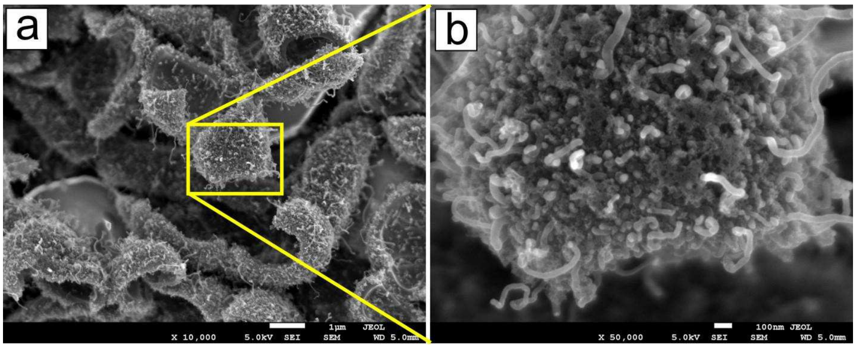

Fig. 3. SEM micrographs of CNT film surface.

The surface of film after modification in second step is presented in Fig. 3. Obtained films were composed of carbon nanotubes containing Ni nanoparticles in the top of nanotubes. Layer by the CVD process as a result of thermal stresses cracked in many places (Fig. 3a). These fragments of layer were slightly folded, so the actual layer surface is much greater relative to the surface of the substrate on which it is applied. On the film surface a large amount of carbon nanotubes of varying length and strongly defected are visible (Fig. 3b).

Figure 4 shows the film surface obtained in the third step of production process. The carbon nanotubes visible on the surface are much thicker because they are coated with Pd–C film in the PVD process. Also in this case palladium nanoparticles are invisible in SEM observations due to very small size.

The exact structure of such a layer was revealed only in TEM studies. The film is composed of carbon nanotubes

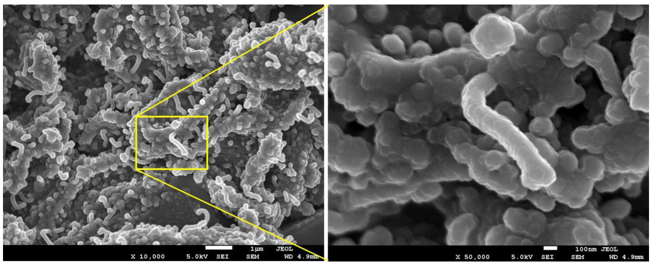

Fig. 4. SEM micrographs of C–Ni–Pd film surface.

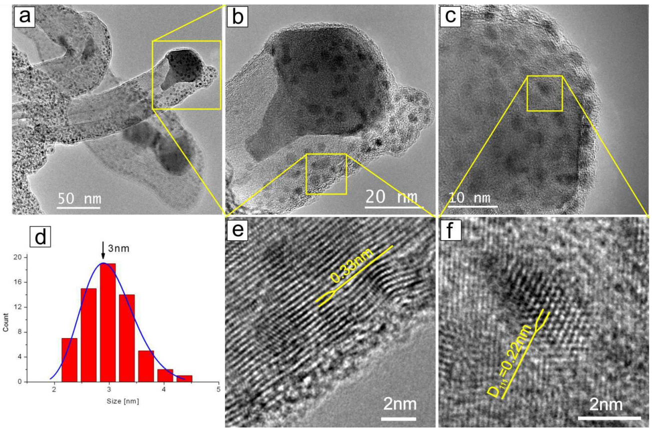

Fig. 5. TEM micrographs of CNT surface: (a–c) the end of carbon nanotube — visible small Pd nanocrystallities and bigger Ni nanoparticle, (d) histogram size of Pd nanocrystallities, (e) graphite shells, (f) columns of atoms in the single Pd nanocrystallite.

containing Ni nanoparticles inside of the topmost part of nanotubes. The top position of Ni nanograin is a result of CNT tip-growth mechanism [30].

The CNTs are built of graphite shells (Fig. 5b,e) with 0.33 nm interplanar spacing. TEM studies have shown that CNTs are decorated with very small nanoparticles of Pd with an average size of 3 nm (Fig. 5d). To determine the size of Pd nanoparticles, a diameter of circles circumscribed on TEM-image with Pd nanoparticles were measured. The most representative part of the image was chosen. This image contained more than hundred Pd nanoparticles. They have a crystalline structure. In this figure the column atoms and the interplanar spacing $d = 0.22$ nm characteristic for Pd (111) were shown — Fig. 5f.

The results of the EDX analysis from the points selected in Fig. 6a in the form of the EDX spectra were presented from left side in Fig. 6b–d. The analysis along the line marked in Fig. 6a has shown that this line crossed the fragment of the carbon nanotube with small Pd nanocrystallities and greater, oval Ni nanoparticle. Figure 6e showed the changes of the concentration of C, Ni, and Pd along the marked line.

Pd nanocrystals were identified by the microanalysis method (Fig. 6b). Such form and properties of prepared films allows applying these films as sensors for gaseous compounds [31, 32].

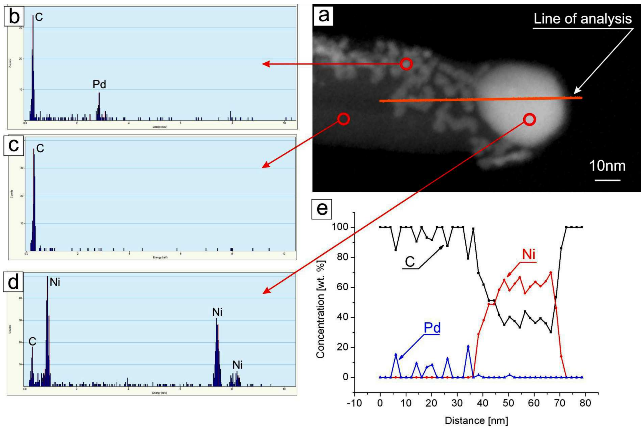

Fig. 6. Results of EDX measurements: (a) STEM micrograph, (b–d) EDX spectra, (e) change the concentration of elements along the line of analysis marked in Fig. 6a.

4. Conclusion

The three components films built of CNTs decorated with Pd nanocrystal (with 3 nm in average size) were prepared by originally elaborated method. It is a simple and cheap method that does not require complex and expensive equipment. These films are composed of CNTs decorated with palladium nanograins with average sizes 3 nm. Inside multiwall CNT big (more than 10 nm in size) Ni nanograins are placed.

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