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PREPARATION AND PROPERTIES OF BARIUM STEARATE MULTILAYERS WITH CARBON NANOTUBES, MANGANESE PORPHYRIN AND SILVER NITRATE

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Barium stearate multilayer samples have been deposited by the Langmuir-Blodgett technique. Carbon nanotubes have been added in the deposition solution. The structural properties have been studied. The effect of the doped multilayers has been tested against the solution of ammonium nitrate in water. The effect of (5,10,15,20-tetraphenyl)-porphinato manganese (III) chloride, (MnTPP)Cl, on the multilayer sample has been tested. The change of resistivity of the multilayer samples modified by manganese porphyrin, as a function of the ultraviolet radiation has been discovered and investigated. The increase of the resistance during irradiation is a reversible process, although a slow one. This effect could give a basis for applications in UV sensors and switches. Finally, a photo-resistive effect (induced by UV light) has been discovered in Barium stearate layers doped by silver nitrate.

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1. Introduction

The nanocarbon tubes become more and more used in applications due to their special properties related to electrical conduction and chemical affinity for various chemical species [1]. The Langmuir-Blodgett films of various compositions are prospective materials to be used as substrates for active species appropriate for chemical and biochemical sensing [2] and are suggested for drug delivery systems [3].

The ordered lattice of the long chain alkylic molecules are ideal host for various chemical molecules. On the other hand the embedded molecules can change drastically the surface of the package of the alkyl molecules and alter the chemically and physical properties (as e.g. the electrical resistance). Intensive studies are carried out in order to evidence the properties of the the nanotubes and fullerenes [4-9] with the purpose to be mixed in LB layers and to reveal the fine chemistry of these systems, thus opening the way to applications in biomedical field.

Combination of chalcogenides nanotubes and carbon nanotubes has been modeled as alternative to carbon nanotube sensing systems [10]. Intercalation of inorganic fullerene-like nanoparticles and nanotubes has been studied by Kopnov and Tenne [11]. Special Y - junction nanotubes have been discussed by Yazdani and Bahrami [12].

2. Materials and methods

Thin multilayer films based on barium stearate molecules have been obtained from stearate powder p.a. (Sigma-Aldrich) dissolved in benzene. Carbon nanotubes have been purchased from Alfa Aesar. They are 1.5 micrometer long and with small diameters. From the

Raman spectra has been deduced the rough composition of the nanotubes in conducting and not conducting components. The fraction of the conducting nanotubles is around 25 % mol as estimated from Raman spectra. Ammonium nitrate is a technical grade substance. Silver nitrate is of p.a. purity.

In this paper we show the preparation and sensing properties of the barium-stearate LB films doped by carbon nanotubes, porphyrin or silver nitrate with the aim to use them in applications.

The synthesis of *(5,10,15,20-tetraphenyl)-porphinato manganese (III) chloride* (MnTPP)Cl was done by metallation of the porphyrin free ligand in ethanol at porphyrin: manganese ratios of 1:20-1:30 and previously reported [13]. Porphyrin free ligand, tetraphenyl-porphyrin, was obtained by Adler method [14] and fully characterized [15].

The apparatus used for preparing the Langmuir-Blodgett multilayers is a double-trough KSV 5000-3 system.

Test solutions have been prepared by stirring the solid powder in water (NH_4NO_3) in preestablished concentrations.

UV irradiation has been performed with a medical UV lamp made by Electrotehnica-Bucharest, having the main emission lines in the range of 330-340 nm at the power density of 116 $\mu W/cm^2$.

AFM images of carbon nanotubes have been recorded with an SPMNTEGRA Prima microscope in the non-contact mode.

The resistances have been monitored using a Keithley 2000 multimeter.

The X-ray diffraction diagram has been recorded with a Bruker D8 Advance diffractometer, with $Cu_{K\alpha}$ radiation.

Fig. 1 shows the AFM image of dispersed carbon nanotubes. The diameter of a nanotube is ~10 nm.

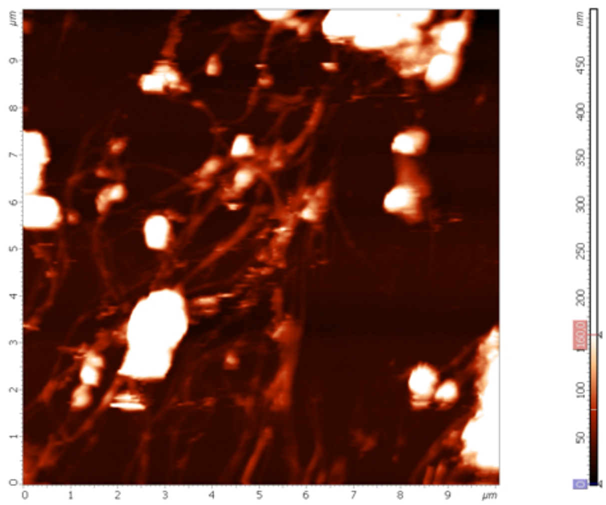

Fig.1 AFM images of carbon nanotubes.

3. Results

Multilayers with 5 barium-stearate layers have been prepared with control of the pressure-area curve and uniform extracting of the sample support from water. The substrates were microscope glass slides and, also, ceramic supports provided with metallic contacts. The carbon nanotubes have been introduced in the initial solution of stearate molecules in benzene. Two concentrations of carbon nanotubes have been prepared on ceramic supports. The LB deposition has been made onto special ceramic sensor substrate provided with platinum contacts.

The following test solutions of ammonium nitrate in water were prepared at the following concentrations: 1.5%; 3.5%; 6%; 9%; 12%; and 15%. The results obtained are shown in Fig. 2.

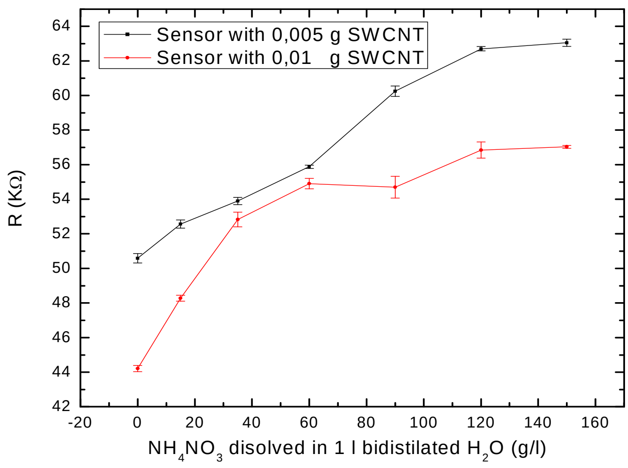

Fig.2 The plot of the resistance of thesensor immersed in the test solution as a function of ammonium nitrate concentration for two sensing bodies with different concentration of carbon nanotubes.

The increase of the electrical resistance with ammonium concentration follows approximately a linear dependence. The slope of the variation of the resistance with the ammonium nitrate concentration is 0.093 kΩ/(g/l). The sensor with low nanotube concentration reveals a more linear behaviour. For this sensor the sensitivity to ammonium nitrate is S=3.9% for 1.5% concentration of NH_4NO_3 and S=24% for 15% concentration variation of NH_4NO_3. This means that this sensor can detect concentrations as low as 0.1 g/l with high accuracy.

The metallo-porphyrin-doped sensors show an unusual behaviour of the resistance under the action of the UV-radiation. In identical conditions the resistance of the sensor increases along a curve with the tendency to saturation for increasing times of irradiation (see the Fig. 3). The resistivity increase and saturates after 3-4 minutes. The rapid increase of the electrical resistance for low irradiation time suggests a possible application of the sensor for threshold switching of an electrical circuit. One of the problems of this type of switch is the stability of the resistance values. The other problem is the slow recovery rate to the initial value of the resistance. The reset time of the sensor is approximately 24 hours.

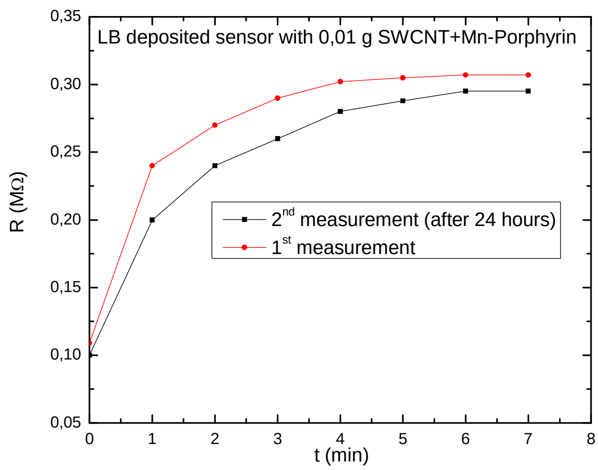

Fig. 3 The effect of UV radiation of the sensor based on nanotubes and Mn-porphyrin.

Finally, we have prepared in the same conditions barium stearate multilayers with silver nitrate. The concentration of the nitrate has been established to 1% g/l.

We have compared the structure of the Barium-stearate layer with carbon nanotubes and silver nitrate with the same sensor without nanotubes but with silver nitrate. The most interesting structural feature of the system with silver nitrate is the presence of two phases with lamellar structure, one corresponding to the pure barium stearate structure (Fig. 4), the other being still unidentified.

The nanocarbon phase seems to prevent the formation of the secondary phase in the multilayer LB sample.

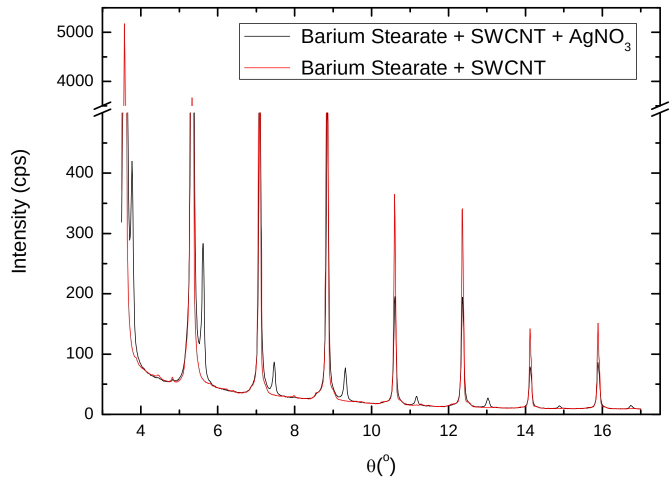

Fig. 4 The X-ray diffraction pattern of the multilayers with carbon nanotubes and without $AgNO_3$ and multilayers with $AgNO_3$ layers

If the barium stearate multilayers covered by nanotubes and $AgNO_3$ are deposited on a ceramic support, provided with platinum electrodes, is tested against the UV radiation, then an important sensitive effect is observed. The electrical resistance increases abruptly when the irradiation time increases. Fig. 5 shows the results. Unfortunately after switching off the UV - light the resistance does not recover to the initial value immediately. Several hours out of work maintenance are necessary for complete recovery. Further work is necessary to understand the phenomenon and to get a rapid switch accompanied with rapid reaching of the initial state.

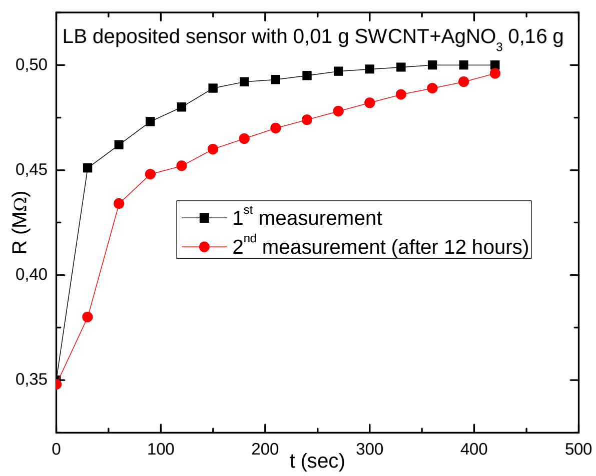

Fig.5 The effect of UV radiation of the sensor based on nanotubes and $AgNO_3$

The special feature of the system with $AgNO_3$ warrants the application of these multilayers for biosensors.

4. Conclusions

Complex multilayers have been prepared by the Langmuir-Blodgett method. The sensing properties of the films of Barium stearate doped by carbon nanotubes have been tested. A strong resistivity effect versus ammonium nitrate concentration in water has been revealed. The sensor resistivity increases nearly linear with the salt concentration. The porphyrin doped multilayers show a strong effect of resistivity change under the action of the UV radiation. A new prospective material based on barium stearate and $AgNO_3$ has been revealed. A photoresistive effect was discovered, when the sensor is illuminated by UV light. Further studies are necessary to reveal the possibility of application of the system with $AgNO_3$ as chemical sensor.

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