Journal of Ovonic Research Vol. 17, No. 4, July - August 2021, p. 405 - 410

Multilayer Langmuir-Blodgett thin films studies for chemical sensors development

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This paper presents the study of the development of complex organic materials deposited by the Langmuir Blodgett technique. We have synthetized Langmuir Blodgett multilayers for the recognition of toxic chemicals in the air and / or ultraviolet radiation. The sensitive materials are based on multilayers of stearic acid metal salts combined with nanocarbon and metalloporphyrin structures. We prepared and obtained by the Langmuir Blodgett method films with nano-metric thicknesses combined in different concentrations of metal salts of fatty acids, Nano carbon structures and metalloporphyrins. Further we have characterized and tested the materials obtained for the sensitivity and selectivity of multilayers under the influence of various toxic gases and / or ultraviolet radiation obtaining high results in the field of sensors.

(Received December 18, 2020; Accepted August 30, 2021)

Keywords: Langmuir-Blodgett, Thin films, Spectroscopic Ellipsometry, Carbon Nanotubes, Chemical Sensors

1. Introduction

Chemical sensors are available in many practical applications but their sensitivity and selectivity are high only for certain substances. Despite the need for a highly sensitive material for CH4 detection, none of the available sensors have a sensitivity below 1 ppm. The selectivity of sensors in the case of gas mixtures is also a very challenging issue.

Interest in environmental pollutants as well as their monitoring has increased considerably. Nitrogen oxides, such as NO and NO2, are typical environmental pollutants. There is a very high demand for smaller, cheaper sensors with high sensitivity and selectivity on these gases. Carbon nanotubes appear to be new sensitive materials in gas detection with outstanding results at room temperature, rapid response and selectivity. [1, 2]

Single-walled carbon nanotubes functionalized for example with poly (ethyleneamine) have been used successfully in the composition of NO2 sensors. [3,4] Nitrogen oxide, NO, was first oxidized to NO2, which was then passed through a single-walled network of carbon nanotubes in a field-effect transistor device, thus inducing changes in the electrical conduction of nanotubes.

Porphyrins have an amazing adsorption capacity, in addition they are characterized by high selectivity and sensitivity that I recommend in sensing systems. Selectivity of these types of materials is closely linked to weak bonds (Van der Waals bonds and hydrogen bonds), porphyrins can create stronger bonds due to the coordination of analytes. An example of the interference of these types of double interactions, which generates the nonlinear adsorption isotherm, is the specific π - π interaction between the aromatic systems of porphyrin and aromatic analytes, such as benzene [5].

Carbon nanotube networks can be functionalized with different agents that can induce better performance characteristics, such as selectivity, sensitivity, etc. [6-9]. The use of transistor-field carbon nanotubes as light detectors has recently been reported. [10-11].

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2. Materials

Thin organic films are an important source of information, having practical applicability for sensors, detectors and components of electrical circuits. Thin organic films can be transferred to a solid support by various techniques such as evaporation, adsorption, self-assembly or by the Langmuir-Blodgett thin film deposition technique.

By spreading a fatty acid solution on the surface of a liquid subphase, a Langmuir monomolecular layer is obtained. To obtain the Langmuir layer on the surface of the water, an amphiphilic, water-insoluble substance is usually used, which is spread as a solution in a volatile solvent. After the solvent has evaporated, the fatty acid molecule will be oriented with the hydrophilic head towards the water surface, while the hydrophobic tail will be oriented more or less perpendicular to the water surface.

Preliminary tests were performed to obtain a homogeneous solution of carbon nanotubes functionalized with barium stearate molecules, and doped with metalloporphyrins. The addition of a functionalizer, namely the surfactant based on dodecyl-benzene sulfonate followed by 30 min ultrasound led to a good dispersion, which is relevant for the stability of the colloidal solution.

The nanotubes used in the preparation of the solutions were purchased from Alfa Aesar. The barium stearate used comes from Strem Chimicals and the metalloporphyrins used, namely manganese porphyrin and iron porphyrin are from Aldrich. For the preparation of the colloidal solution compatible with the deposition of Langmuir-Blodgett layers, benzene was used for high purity analysis (99.8%).

3. Methodology

We prepared new structures based on barium stearate doped with carbon nanotubes and activated with metalloporphyrins.

Simple layers of barium stearate were prepared by the Langmuir-Blodgett method using the KSV 5003 apparatus. The thin films consist of 5 Langmuir-Blodgett-type layers deposited on glass supports. We prepared Langmuir-Blodgett layers under and under identical conditions with and without carbon nanotubes. Samples of carbon nanotubes and metalloporphyrins were also prepared.

In order to follow the behavior of the prepared solutions, before the transfer on glass supports we performed with the help of mobile barriers within the same cycle a compression to the optimal level for transfer on the support, followed by a decompression to the initial level, and finally a return at the maximum compression level. In this way we were able to study the effect of hysteresis to understand the effect of carbon nanotubes on the properties of complex layers.

After characterizing the material of interest deposited on glass supports, the same solutions were transferred and sensor supports in order to test the sensitivity and selectivity of Langmuir-Blodgett multilayers. Thus, with the help of the Langmuir - Blodgett type deposit installation, the layer-by-layer transfer of the material was made on a commercial support made of a ceramic plate provided with platinum electrodes in the comb system.

4. Results and discussion

X-ray reflectometry: The quality of the packaging of the complex layers in each multilayer was determined using X-ray reflectometry. For this we used a Rigaku SmartLab diffractometer equipped with Cu anticathode, parallel incident beam configuration and Kα radiation (λ = 1.54178 Å) and the HyPix-3000 2D Hybrid Pixel Array Detector (in 0D mode). Figure 1 shows the reflectograms for multilayers based on barium stearate.

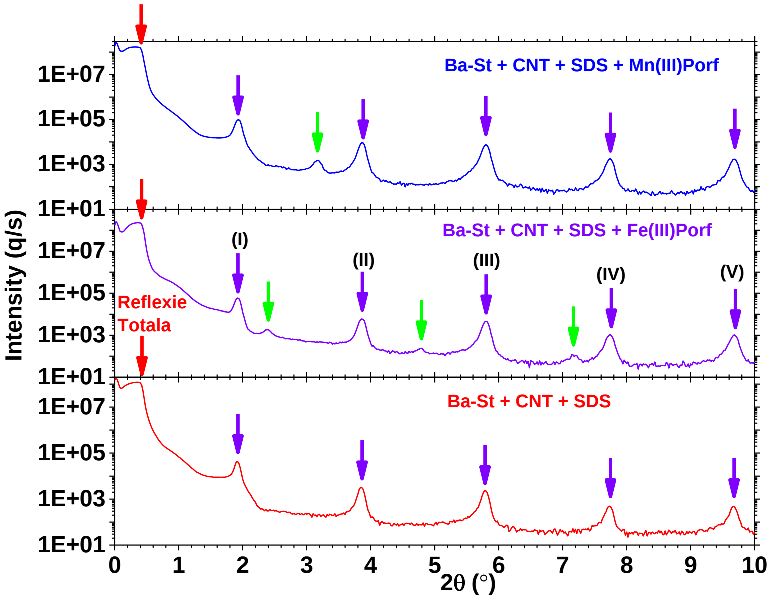


Fig. 1. Reflectograms for barium stearate multilayers. The purple arrows indicate the majority phase, the green ones indicate the minority phase.

The packing constant (average layer thickness) for the porphyrin-free multilayer is 4.6 nm. When Fe (III) -porphyrin is present in the component of each layer of the multilayer, it is found that we generally have the same average layer thickness, with the mention that there is a minority packaging with an average layer thickness of only 3.7 nm indicated in the figure by green arrows .

The same situation for the incorporation of Mn (III) -porphyrin, only that the minority packaging (indicated in the figure by the green arrow) has an average layer thickness of 2.8 nm. These minority packages appear to be defects in the packaging of Barium Stearate due to the presence of carbon nanotubes whose average diameter is 1.6 nm.

UV-VIS transmission: The optical transmission spectra of Langmuir-Blodgett multilayers was measured. The two spectra were compared in order to signal the presence of carbon nanotubes and metallic porphyrins in the structure of LB multilayers. A UV-VIS spectrophotometer from Perkin Elmer, NIR Lambda 1050, was used for this mesurment.

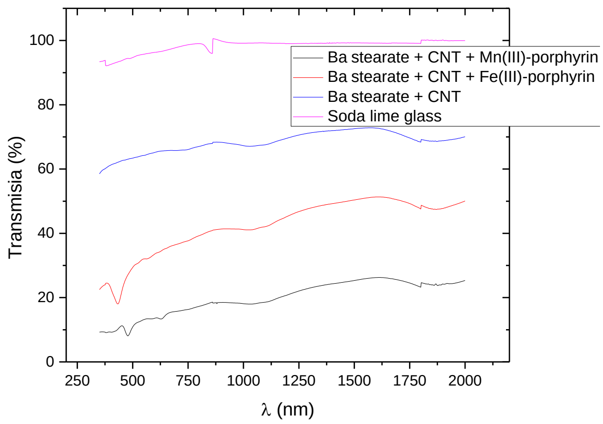


Fig 2. Langmuir-Blodgett multilayer optical transmission spectra

Unlike the backing layer, the presence in the spectrum of the sample with carbon nanotubes, carbon nanotubes and Mn porphyrin and that with carbon nanotubes and Fe porphyrin of a maximum absorption, in the wavelength range 1000-1100 nanometres, was identified being more pronounced in the Fe porphyrin test. Also noteworthy is the increase in absorption at long wavelengths above 1600 nm.

The transmission changes for the 3 thin films are due to the presence of Fe and Mn metalloporphyrin. Thin films containing Mn metalloporphyrin have a lower percentage of transmission than thin films containing Fe metalloporphyrin, and much lower than simple film not doped with metalloporphyrins, which lead to further studies for development of optical sensors.

Ellipsometry: Figure 3 shows the refractive and extinction coefficient of LB multilayers deposited on glass support. A UVISEL Spectroscopic Ellipsometer from HORIBA - France with a spectral range of 190-20100 nm was used.

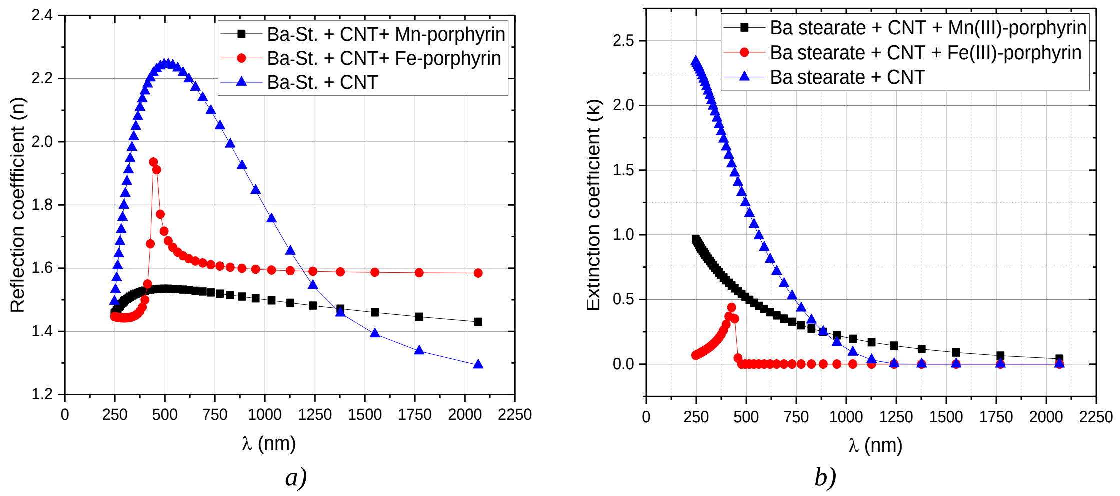
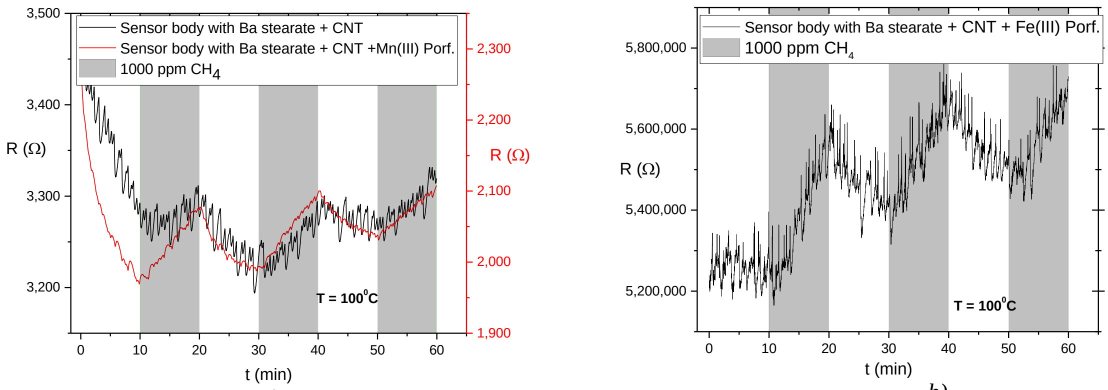


Fig. 3 a) Reflection coefficient (n),
b) Extinction coefficient (k) for the Langmuir-Blodgett multilayers

A model according to the measured ellipsometry parameters was made using DeltaPsi ver. 2.7.0 software. The modelling was performed using the Tauc Lorentz formula (oscillator) in order to determine the thickness of the thin films, the refractive index "n" and the extinction coefficient "k" in the range 190-2100 nm for different thicknesses of the 3 thin films deposited on the substrate glass. The model used consists of a main layer of Barium Stearate and carbon nanotubes deposited on the glass substrate with a layer of surface roughness. The surface roughness was modelled by mixing the optical constants of the material surface and gaps (on average: in relation to 90% material and 10% gaps (air)). The differences of the refractive index "n" and the extinction coefficient "k" are due to the presence of Fe metalloporphyrin and Mn metalloporphyrin and thus by changing the thickness or composition of thin films optical sensors can be developed with applications in optoelectronics - photonics. The observed changes in the refractive index "n" and the extinction coefficient "k" are associated with the structural change in barium stearate and carbon nanotubes induced by the doping of Fe metalloporphyrin and Mn metalloporphyrin rather than the effect of thickness change them.

Gas Sensitivity Tests: We prepared LB multilayers of barium stearate and carbon nanotubes and LB multilayers of barium stearate and carbon nanotubes and metalloporphyren of Mn and Fe, transferred to special ceramic supports for the detection and measurement of methane gas (CH4). The sensor support consists of an alumina plate provided, on one side, with platinum contacts, on which the active material is deposited, and on the other side, with an electric heating system separate from the contacts for monitoring the resistance to the surface covered with active material. The ceramic sensor body is an essential element for detecting resistance changes due to the action of toxic gas.

Figure 4 illustrates the sensitivities obtained in the presence of methane gas CH_4 at a temperature of 100 ^oC of the 3 LB multilayers deposited on sensor bodies.



a) *b)*

Fig 4. Variation of the electrical resistance of the sensor under the action of methane gas
a) Sensors with barium stearate and carbon nanotubes and barium stearate and carbon nanotubes and manganese porphyrin;
b) Sensor with barium stearate and carbon nanotubes and Fe porphyrin.

No sensor responded to room temperature or concentrations below 1000 ppm CH_4 introduced into the gas mixing chamber. The testing was done for one hour in which the first 10 minutes the sensor was in a controlled atmosphere of synthetic air and after 10 minutes it was introduced in the premises 1000 ppm CH4 for 10 minutes, the procedure being repeated 3 times.

A slight effect of increasing the electrical resistance under the influence of CH4 can be observed for 10 minutes for each sensor (Fig. 4a). The effect is more pronounced in the case of the barium stearate sensor with carbon nanotubes and doped with manganese metalloporphyrin. The sensor with barium stearate, carbon nanotubes and manganese porphyrin has a lower resistance than the one not doped with metalloporphyrins and also a steeper slope of the response under the influence of CH4.

It can be observed in the case of the sensor deposited with LB multilayers with barium stearate and carbon nanotubes and iron porphyrin (Fig. 4b) a general increase of the electrical resistance of the investigated multilayers. And in this gas there is a slight increase in resistance in the range of methane gas, followed by a decrease, which can mean a desorption of the gas on the surface of the material. The resistance increase slope is the highest in the case of this sensor doped with iron porphyrin.

5. Conclusions

Regarding the development of complex organic materials by Langmuir-Blodgett (LB) technique and sintering of LB multilayers for the recognition of toxic chemicals in air and / or ultraviolet radiation, we achieved all the objectives and highlighted the possibility of using multilayers. LB in the production of chemical sensors.

Solutions based on barium stearate and carbon nanotubes were prepared, doped and undoped with manganese and iron metalloporphyrins. Subsequently, they were deposited by the Langmuir-Blodgett method on glass supports and characterized structurally and optically. Subsequently, the prepared solutions were transferred to sensor bodies in order to test the sensitivity of Langmuir-Blodgett multilayers under the influence of methane gas.

We have highlighted an effect of increasing the electrical resistance under the influence of 1000 ppm of methane gas (CH4). The effect of increasing the electrical resistance is more pronounced in the case of the two sensors doped with metalloporphyrins compared to the one without metalloporphyrins.

Comparing the sensors doped with metalloporphyrins, it can be seen that the one with iron porphyrin is more resistant and has a steeper slope of increase in resistance under the influence of CH4 compared to the one doped with manganese porphyrin.

We note the need of further research in order to optimize the material for use in development of toxic gas detectors.

Acknowledgements

This work was supported by the Romanian National Authority for Scientific Research CCCDI-UEFISCDI, through Core Program - project PN 21N/2019.

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