PACS 07.07.Df, 68.35.bp

Fullerene and fullerene-aluminum nanostructured films as sensitive layers for gas sensors

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Abstract. The responses of quartz crystal microbalance (QCM) sensors coated by fullerene and fullerene-aluminum films to ethanol and water vapors are investigated. The possibility of controlling the adsorption properties of such films by inserting the aluminum and by ultraviolet irradiation that changes the film morphology in a definite way is demonstrated.

Keywords: Electronic Nose (QCM), fullerene nanostructured films, ultraviolet irradiation.

Manuscript received 08.04.09; accepted for publication 14.05.09; published online 30.06.09.

1. Introduction

A wide variety of nanostructured materials are among the most important objects of investigation in modern science. In particular, they are of significant interest for gas sensing applications. Any sensor system is characterized by certain functionality and selectivity profile, which defines its application area. Since the adsorption properties of sensors depend on their surface morphology and chemical composition, the investigation of new materials with well-defined surface structure is of great importance.

In this work, we discuss the advantages of using the fullerenes and fullerene-aluminum films as sensitive coatings for gas sensors.

Fullerenes and fullerene-based compounds are promising materials for various applications in analytical chemistry. They are used as chromatographic stationary phases, as electrochemical sensors based on their activity as electron mediators, as sorbent materials in continuous flow systems [1]. Great attention is paid to the use of fullerene and fullerene-based films as sensitive layers for chemical sensors. A lot of results concerned with the investigation of adsorption properties of such films towards various organic and inorganic compounds were reported in recent years. High sensitivity of mass-sensitive sensors coated by C_{60} film to humidity was shown in [2], while in the work [3] the humidity was considered as a negative factor that decreases the electrical response of the C_{60} film on hydrogen. The possibility to use C_{60} and their derivatives to detect various organic molecules like amines, dithiols, alkynes and 1,3-dienes (chemisorption) and alcohols, aldehydes, carboxylic acids (physical adsorption) as well as metal ions and anions with good reproducibility and detection limit was demonstrated in the work [4]. C_{60}-based coatings of mass-sensitive biosensors are useful for the detection of hemohlobine, immunoglobulin G [5] and for detection of anti-hemoglobin and anti-myoglobin antibodies [6]. The perspectives of using the two-component films composed of fullerenes and some transitive metals for electrochemical sensors were discussed in the work [7].

It is known that morphology of fullerene and fullerene-based films can be changed in the definite way by creation of mixed metal-fullerene layers [7, 8]. Another promising way of surface modification is application of some external influence, for example, illumination. The morphology and composition of photopolimeryzed C_{60} films was reported in [9].

In this work, the adsorption properties of fullerene C_{60} and fullerene-aluminum films towards ethanol and water vapours are investigated and discussed.

2. Experimental procedure

Mass-sensitive sensors based on quartz crystal microbalance (QCM) were used for the investigation of adsorption properties of fullerene and fullerene-aluminum films. Sensors were put into the flow-type chamber. Saturated vapour of analyte passed through the chamber with a constant speed, argon was used as a carrier gas. The QCM oscillating frequency shift due to adsorption of analyte molecules on their surface was measured [10].

Fullerene and fullerene-aluminum films were deposited by thermal evaporation in vacuum directly on the electrode of QCM. Since the sublimation temperature of fullerenes is less than the aluminum evaporation temperature, there were used two different evaporators.

Morphology of films was studied using atomic force microscopy.

3. Results and discussion

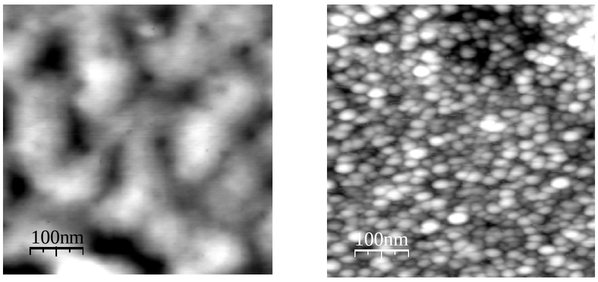
The difference between fullerene and fullerene-aluminum films can be seen from the AFM images shown in Fig. 1. The introduction of aluminum decreases the typical cluster size from 70-100 nm for the fullerene film down to 20-30 nm for the fullerene-aluminum one. At the same time, the uniformity of the surface is improved. The adsorption properties of two films significantly differ.

The responses of C_{60} film to water and ethanol average 3-5 Hz that is quite low for the adequate measurements (see Fig. 2, curves 1, 3). The sensitivity of C_{60}-Al film is about 55 times higher and totals 208 Hz for ethanol and 167 Hz for water vapour (curves 2 and 4 in Fig. 2). The increase of sensor response can be explained in view of the film structure: adsorption capacity of the nanoorganized metal-fullerene film is higher than that of fullerene film composed of relatively large clusters.

The similar influence on morphology and adsorption properties of C_{60} and C_{60}-Al films has their exposure to UV irradiation. With the increase of exposure time, the characteristic cluster size decreases, the surface becomes more uniform, and its sensitivity to water and ethanol vapours increases.

The dependence of the response for the C_{60}-covered sensor to ethanol on the time of exposure to UV irradiation is shown in Fig. 3.

AFM images of fullerene (a) and fullerene-aluminum (b) films after UV irradiation for 30 min are presented in Fig. 4. After 30 min UV irradiation, the amplitudes of the responses are about 50 to 90 times increased for C_{60} coating and about 2.5 times for the C_{60}-Al one (see Fig. 5).



a b

Fig. 1. AFM images of fullerene (a) and fullerene-aluminum (b) films.

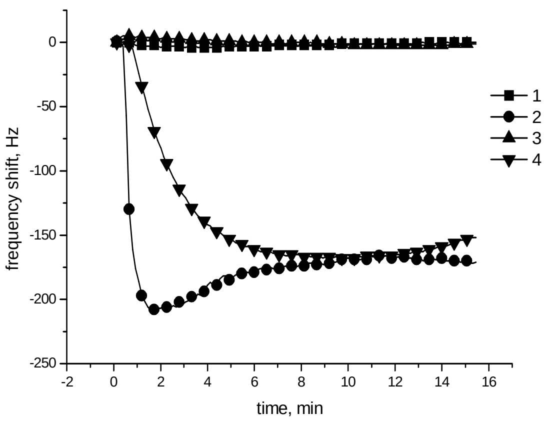


Fig. 2. The response of QCM sensors coated by fullerene (*1* – to ethanol, *3* – to water vapour) and fullerene-aluminum (*2* – to ethanol, *4* – to water vapour).

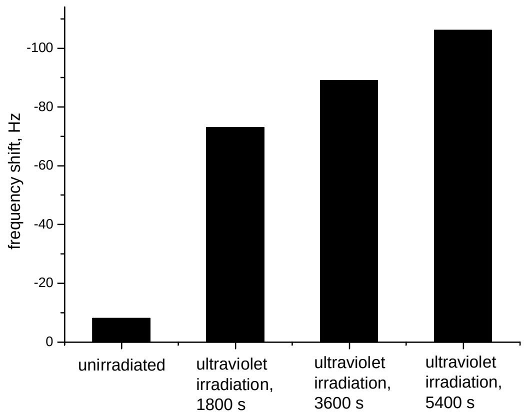
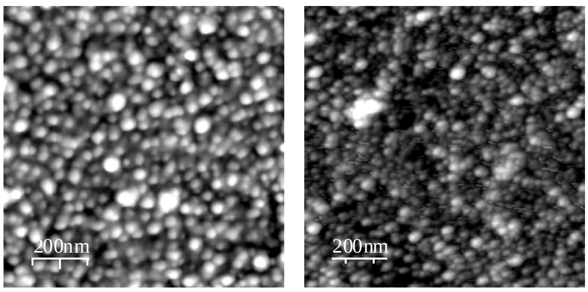


Fig. 3. The dependence of C_{60}-coated QCM sensor response to ethanol vapor on the time of exposure to UV irradiation.



a b

Fig. 4. AFM images of fullerene (a) and fullerene-aluminum (b) films after UV irradiation for 30 min.

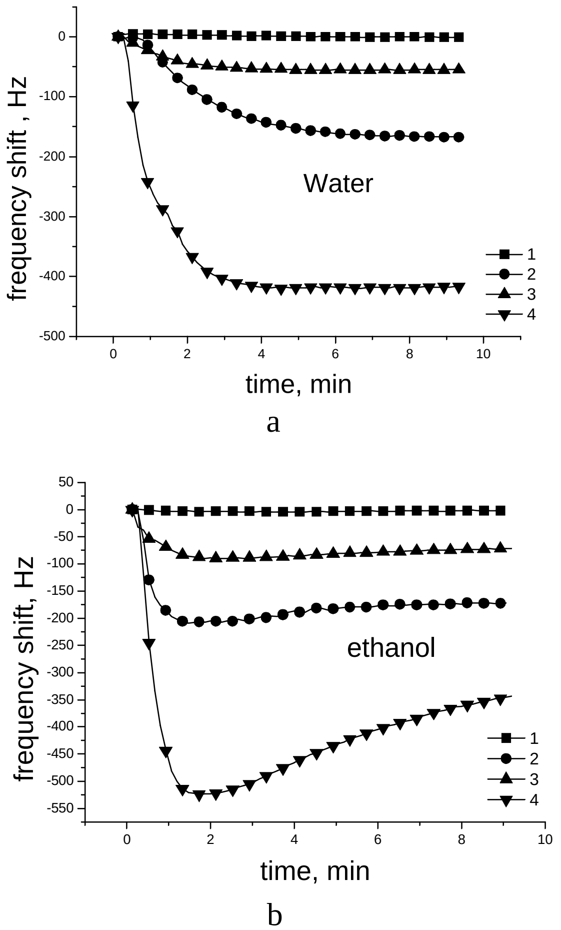


Fig. 5. QCM sensors' responses to water (a) and to ethanol (b) and for fullerene-coated sensors (*1* – before UV irradiation, *3* – after UV irradiation) and for fullerene-aluminum coated sensors (*2* – before UV irradiation, *4* – after UV irradiation).

5. Conclusions

Modification of fullerene films by inserting metal atoms and/or UV irradiation is a promising way to increase the sensitivity of films to some analytes. Besides, the selectivity profile of the C_{60} film can be changed by illumination: the influence of UV exposure on the response amplitudes differs for water and ethanol. Both methods of C_{60} surface modification can be successfully used for the development of sensor arrays for gas analysis.

Acknowledgments

This work was supported by Program of the National Academy of Sciences of Ukraine "Nanosystems, Nanomaterials and Nanotechnologies".

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