ISSN 2669-2023 (print) / ISSN 2538-8959 (on-line) / https://doi.org/10.47459/cndcgs.2022.36

# Structural Characteristic of Fullerene C 60 and its Sorptive Properties

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**Abstract**

The pandemic situation associated with the occurrence of COVID-19 has necessitated the initiation or renewal of research activities aimed at the possibility of using materials that will have very good post-accident properties. One of the materials that have been developed, tested and applied in the past has been materials based on the spherical fullerene C 60 molecule. A microstructure using REM and SEM and sorptive properties of fullerene C 60 for gases of toluene with the employment of a QCM detector has been studied. Obtained micrographs are discussed in relation to a possible spatial arrangement at the molecular level. The envisaged solution aims to develop a sensor that, due to its surface properties, would be useful for the detection of gas and liquid phases of chemical warfare agents and industrial chemicals. It is envisaged that the surface layer consisting of fullerene C 60 will be universally applicable, reusable and low cost and low maintenance.

**KEY WORDS:** *Fullerene C 60, microstructure, nanostructure, SEM, REM, QCM, sorption*

## 1. Introduction – theoretical part

### 1.1 Security framework of the solved problem

The current security situation and environment shows us all that it is not possible to state unequivocally that we live in a secure world. This statement can be based not only on the fact that the possibility of an escalation of conventional military conflict is quite real, but also on the fact that there are still stockpiles of weapons of mass destruction held by states that make no secret of the possibility of their use (or rather misuse). At the beginning of the Russia-Ukraine war, we were informed about the possibility or perhaps even the will to use chemical and nuclear weapons. The dangers of using nuclear weapons in military conflicts do not need to be discussed in detail; protection against their use is very specific and, it must be admitted, not very promising. Rather, the subject of the research presented in this article is an attempt to create conditions for providing hopeful protection against the action of chemical weapons, whose main active component of which are chemical warfare agents. Their action causes very significant loss of life even at low concentrations. Leaving aside the possibility of the use of chemical warfare agents and chemical weapons as such, it is possible to talk about the possibility of leakage of industrial hazardous substances into the environment, of which there is a considerable amount in industrialised Europe [1-3]

All of the above facts lead the researchers to consider what barrier materials will be most effective for protecting not only the chemical specialists of military units and fire brigades, but also the civilian population. Currently, there are several very good and technologically applicable materials that meet the requirements for providing quality protection from the effects of toxic substances while meeting very stringent tolerability criteria in terms of medical requirements. A very modern area is that of nanomaterial technologies, which are now very well-known based on the for example pandemic situation associated with COVID-19 [4-6].

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### 1.2 Fullerene C 60 and its basic properties

The known allotropic modifications of carbon, thus diamond and graphite, have been joined by fullerenes since the end of the 20th century. These substances consist of Cn molecules which are composed of twenty or more carbon atoms, the total number of carbons being always even. Fullerene molecules are also sometimes referred to as clusters. These clusters are polyhedra that are characterized by an almost regular circular shape. The carbon atoms are located at the vertices of the polyhedra.

The surface properties of materials made from fullerene C 60 may predispose them to a variety of applications that can take advantage of the physical and sorption properties of this carbon material. Fullerenes is ranked among the three most stable molecular structures of carbon currently known. Its typical characteristic is that it can occur in spherical, elliptical, tubular or ring shapes. The binding properties of fullerene are also very interesting. The bonding of the carbon atoms in the fullerene shell is mediated by σ bonds always to three neighbours and a weaker π bond whose orbitals stand radially to the shell. This lower binding energy is responsible for the electron properties of fullerenes. The π electrons are freely mobile (delocalized) throughout the fullerene shell, but their density is not distributed uniformly over the surface of the molecule. The greater density is on the double bonds (connecting the five-membered rings), the lesser density on the bonds within these rings.

C 60 fullerene is the most abundant member of the so-called fullerene family [7]. Its practical applications have begun to be applied in a wide range of industries that are significantly influencing research into its potential [8]. A spherical fullerene C 60 molecule containing 60 carbon atoms consists of five- and six-member circles of carbon atoms spatially arranged in a spherical shape. Chemically it is a relatively stable and low reactive compound, slightly soluble in water and limited in organic solvents. However, its spatial arrangement assumes that, under suitable conditions, this compound could adsorb gaseous substances [9,10]. For example, metallo-fullerenes with 80 or more carbon atoms which have an atom or several metal atoms in their cavity are known. In this paper, attention is paid to the C 60 microstructure and a suitable method for studying sorption properties of this substance in a gas phase is proposed. In addition to C 60 fullerene, samples of this substance were also tested after amine and chlorine reaction, as well as the sample after gamma irradiation. First, a basic sample of fullerene C 60 has been investigated. Initially, a suitable solvent was used to prepare the detection layer and to examine the microstructure by means of a Transmission (TEM) and Scanning (SEM) Electron Microscope. Of the below-mentioned organic solvents, toluene has proven to be best for this purpose, although it does not exhibit the greatest solubility. Since under normal laboratory conditions, fullerene C 60 dissolves very reluctantly, dissolution has to be accelerated using an ultrasonic bath [11,12]. The resulting solution is red-violet due to solvation, and the fullerene concentration in it is about 3 mg/ml. The figure 1 shows the solubility of C 60 fullerene in an arrow direction.

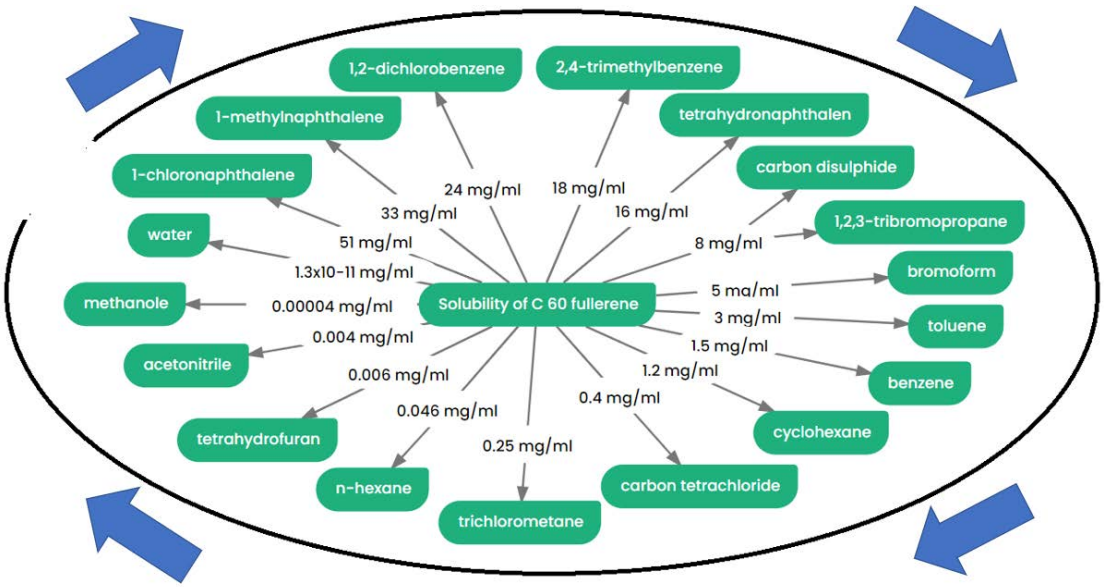



Fig. 1 Solubility of C 60 fullerene in different solvents [source: own elaboration]

As a matrix for studying the micro morphology of the monitored samples by high-resolution electron scanning microscopy, polished quartz plates have been used for use in the semiconductor industry. The basic solution has been then repeatedly dropped onto the polished surface of these plates. After crystallization of the substrate and

subsequent drying, the samples thus prepared have been monitored in an electron scanning microscope with high resolution. It should be noted that the solution for sample preparation for SEM has not been filtered before application, so it could also contain a certain proportion of the original non-recrystallized fullerene. This fact complicated the assessment of acquired micrographs to some extent. The original undiluted sample of fullerene C 60 has been crushed in an agate mortar and used for the study of microstructure with TEM. As can be seen from the pictures, there is also a crystallographic difference between recrystallized and the original sample, each of which can not only have different structural arrangements but also different properties. While SEM provides us with information about the micro morphology of the studied nanostructured formations monitored sample surface, by TEM with high energy of the primary electron beam comes to translucence of the and images characterize rather the arrangement of the nanostructures present in the sample mass [13-15].

Everything that has been stated so far assumes that new and possibly already used barrier materials will be tested using methods and detection techniques that will not only allow their rapid evaluation, but also provide scientifically shared information that can be evaluated across the entire expert community. In order to obtain such information, it is necessary to use specially developed sensors and sensor technologies that are as versatile as possible in terms of their application and highly sensitive in terms of detection efficiency. All these requirements are the subject of very intensive research, with fullerene C 60 being used as a potentially useful material for the formation of a highly sensitive detection layer.

### 1.3 Basic information concerning a QCM detection method

The use of mass detectors and sensors based on the principle of highly sensitive quartz microbalances for the detection of toxic chemicals is now very common. Their typical characteristics are high sensitivity, relatively high versatility, reusability and the possibility of implementing decontamination procedures. The detection of highly toxic substances, such as chemical warfare agents, industrial chemicals and biological agents, requires a number of safety and protective measures, requiring the wearing of personal protective equipment, in particular body surface protection, including gloves. Instrumentation containing mass crystal resonator-based sensors must be adapted to work in personal protective equipment. This adaptation shall be based on the realisation of the sensor robustness requirements of the whole detector, so that it is able to withstand less than gentle handling and handling.

Use of gravimetric microbalance sensors is based on the change of basic oscillatory frequency $f_0$ by adsorption or absorption of molecules from the surrounding gas phase. In the simplest case, this phenomenon can be described by Sauerbray´s equation [16]:

$$\Delta f = -f_0^2 . \frac{c_f}{A_k} . \Delta m, \tag{1}$$

where used symbols mean:
- $\Delta m$ is mass increasing;
- $\Delta f$ is frequency decreasing;
- $A_k$ is a size of crystal´s layered surface;
- $f_0$ is basic oscillatory frequency of the crystal;
- $c_f$ is mass sensitivity.

By the quartz resonator operating in vibratory- shear mode mass sensitivity $c_f$ may reach about 2.3 x $10^{-10}$ g.m$^{-2}$. Resonator with the basic frequency $f_0$ = 10 MHz the detection limit of the detector is equalled to a nano-gram level [17]. Obšel and Dvořáková introduce that with the employment of formula (1) it can count a unit addition of mass $\Delta m$ which - in case of used QCM detector - has reached approximately the value of 6.8 ng.cm$^{-2}$. From the formula (1) also results that the relative change of frequency is proportional to mass change on detector´s surface (quartz).

$$\frac{\Delta f}{f_0} = -\frac{\Delta m}{m}. \tag{2}$$

From equation (2) it is clear that the weight limit depends on the weight of the crystal $m$ for working frequency of the QCM detector with a polymer layer is decisive the thickness of the AT cut crystal, but this rate cannot exceed 20 MHz. This frequency limits the detection limit on the maximum value of 0.1 ng.mm$^{-2}$ of a detector (crystal) active area.

### 1.4 Particular application of fullerene C 60 in terms of the QCM method

A special analytical procedure using QCM, which enables assessing fullerene C 60 sorption properties with nanogram sensitivity, has been chosen for study of its sorption properties. For this purpose, a solution of fullerene C 60 in toluene has also been repeatedly applied dropwise on a metal electrode of the QCM sensor to form a uniform layer thick of several tens of nanometers and a weight of about 100 ng. The response of in this way prepared QCM sensor has been scanned using a special device permitting permanent monitoring of the change of the fullerene C 60 layer in the organic vapor environment, in our case of toluene. A disadvantage of this system is that a new sample must be prepared for each measurement due to the sorption of toluene vapors is not reversible for the fullerene C 60. It has been found up that sorption of saturated vapors of toluene at 25 ºC results in a sorption value of about 20-25 % of the layer weight in static conditions, which corresponds to the conventional carbon adsorbents sorption. However, it appears that this property will have the fullerene C 60 after dissolution and recrystallization, not in the original form. However, this has not been proved successfully to this time.

The genesis of the individual types of fullerenes formation is illustrated very clearly in Figure 1, taken from the Melker´s study [9].

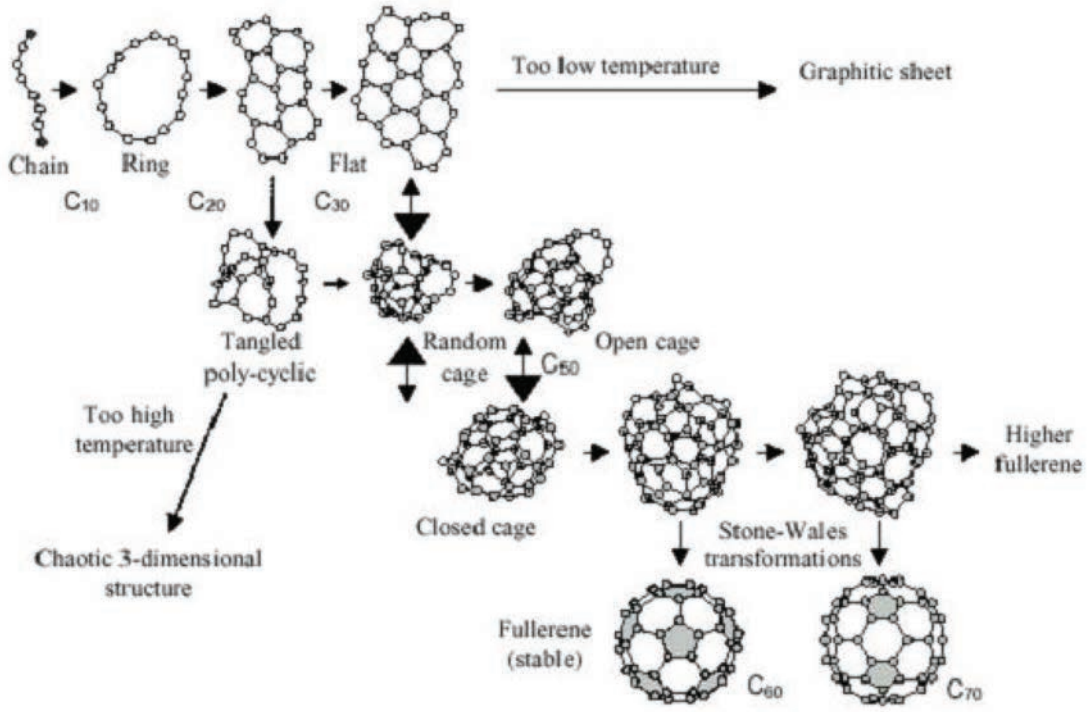
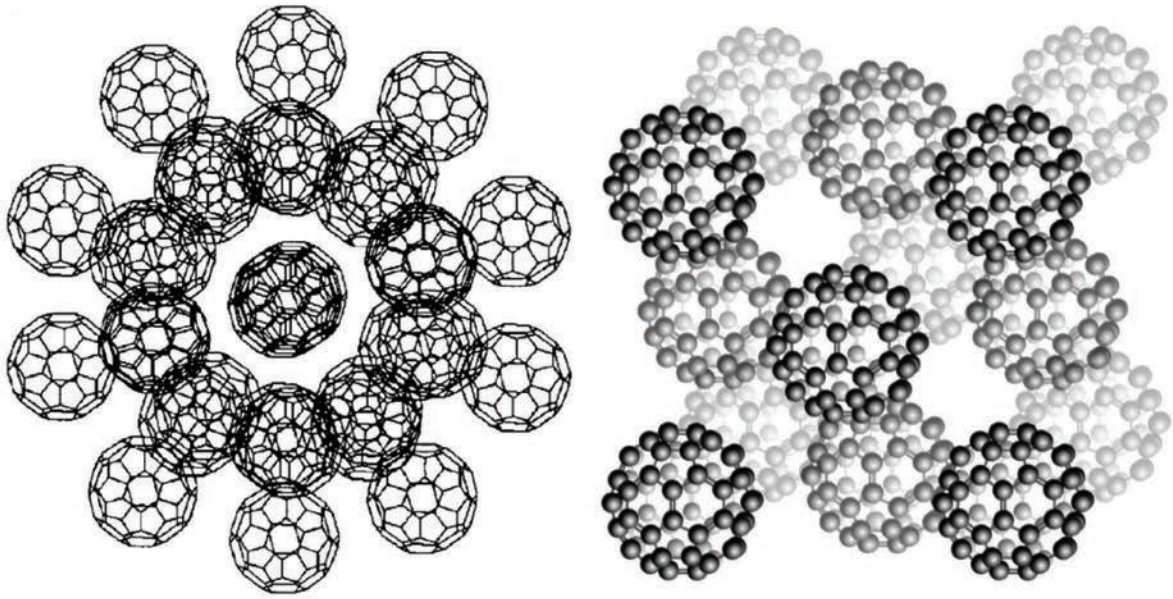


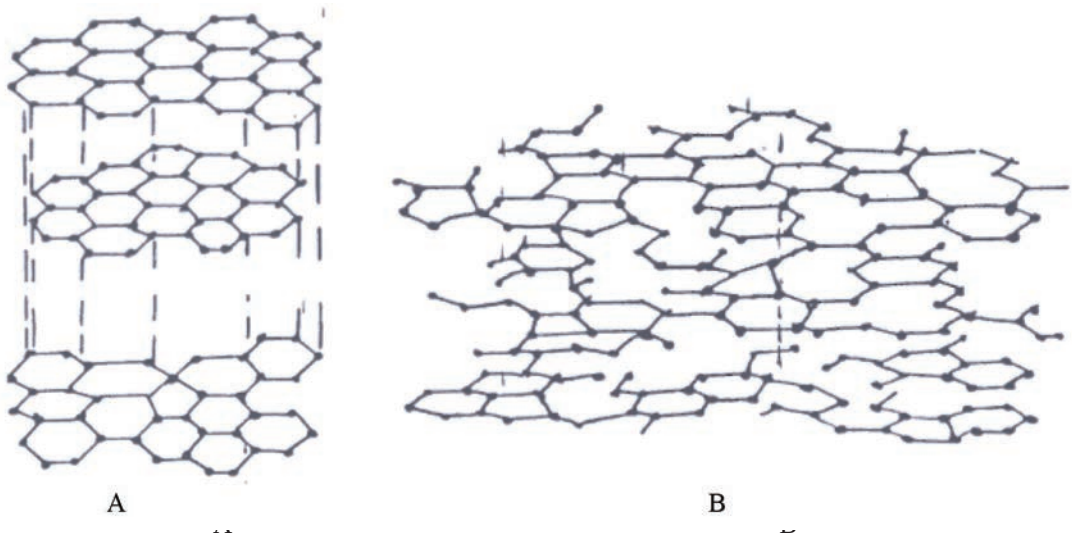

Fig. 1. Scheme of various types of fullerenes preparation

However, the most stable one, fullerene C 60, does not have a simple molecule structure in the solid state. It always clusters into agglomerates with a typical crystallographic arrangement. Figure 2 shows possible agglomerates with a cubic (a) and hexagonal (b) configuration forming the walls of so-called buckyball. This is not a classical graphical or turbostratic structure with the spacing of individual carbon layers in tenths of nanometers (Figure 3) but rather formations whose size is about 14 nm. It is generally stated that for a hexagonal configuration a minimum of 33 base units of fullerene C 60 is required [2,3].



A B

Fig. 2. Supposed cubic (A) and hexagonal (B) arrangement of fullerene C 60 basic molecules



A B

Fig. 3. Graphitic (A) and turbostratic (B) microstructure of graphite and activated charcoal

Another possible variant is the arrangement of fullerene C 60 into a double layer, allowing the formation of hollow spherical formations with many base units (6,000 or more) as shown in Figure 4 [4].

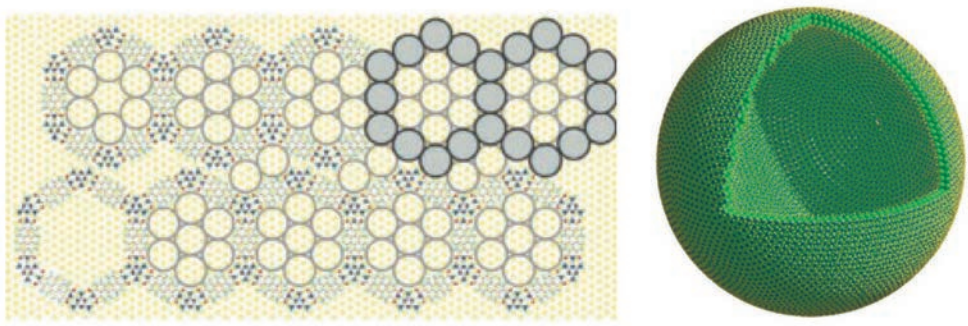


Fig. 4. The two-layered C60 fullerene layout and the possible appearance of the formed ball formation

## 2. Experimental part and discussion of results

The real nanostructure of the studied fullerene C 60 sample is evident from the micrographs in Figures 5-10. From these images, the carbon molecules are layered to form a porous structure with spacing between the layers of about 1 nm.

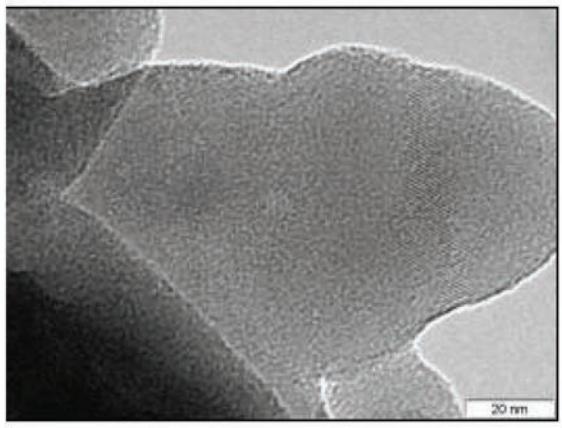



Fig. 5.

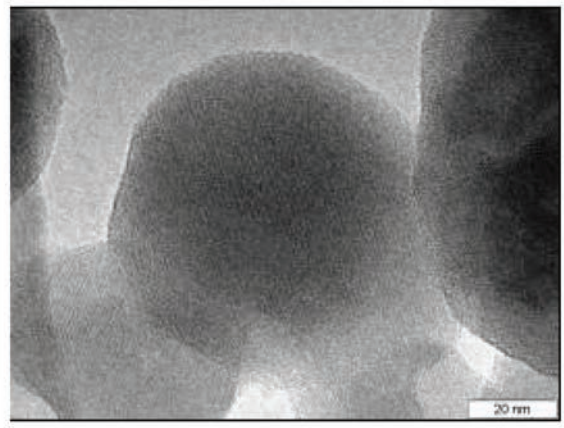



Fig. 6.

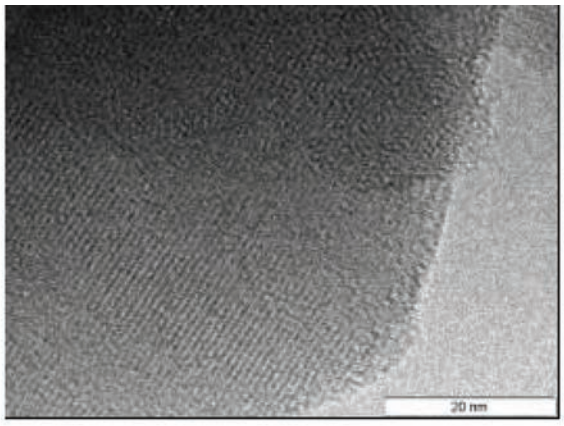



Fig. 7.

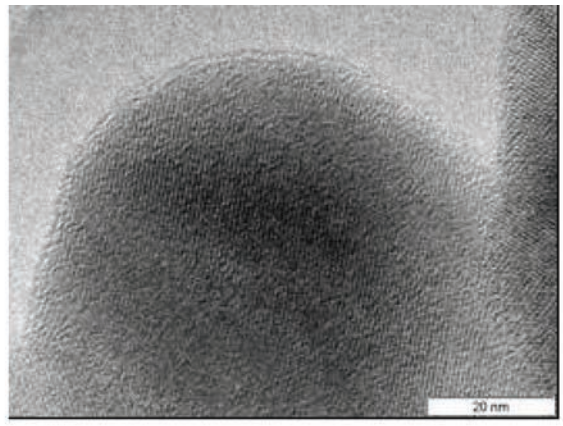



Fig. 8.

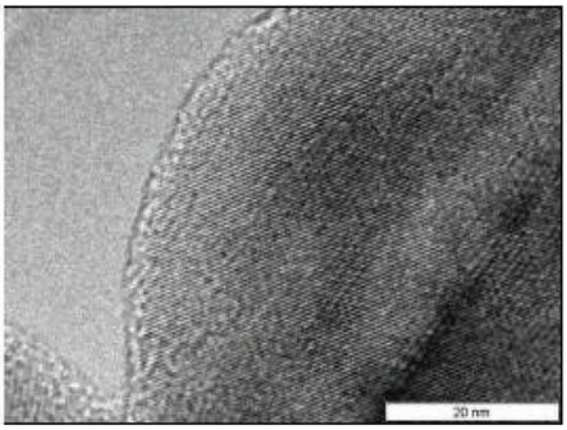



Fig. 9.

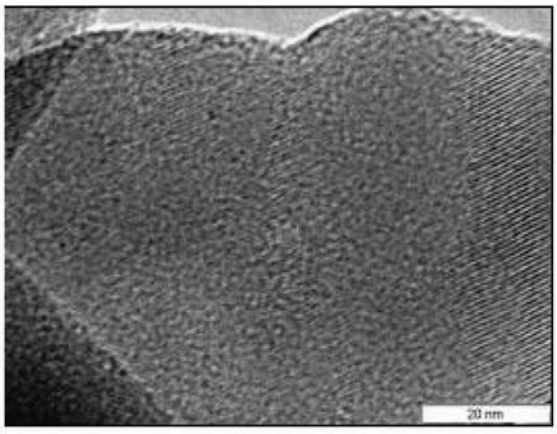



Fig. 10.

It seems that these layers are formed by evenly arranged buckyball molecules which are still spatially cross linked. This would also correspond to the microstructure of the observed fullerene C 60 nanoparticles surface before recrystallization in toluene, as determined by the scanning electron microscope at the Institute of Instrumentation of the Czech Republic Academy of Sciences in Brno (see Figures 11-16). Fullerene C 60 nanoparticles prepared by recrystallization in benzene have rather crystalline pattern (Figures 11 and 12), whereas the fullerene C 60 starting sample forms oval formations (Figures 13 and 14) or clusters of spherical formations (Figures 15 and 16) which are hollow upon closer examination (see Figure 17) with a wall thickness of 80-100 nm.

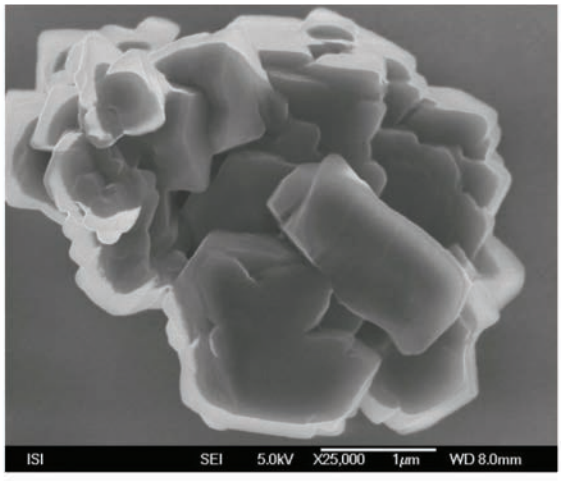



Fig. 11.

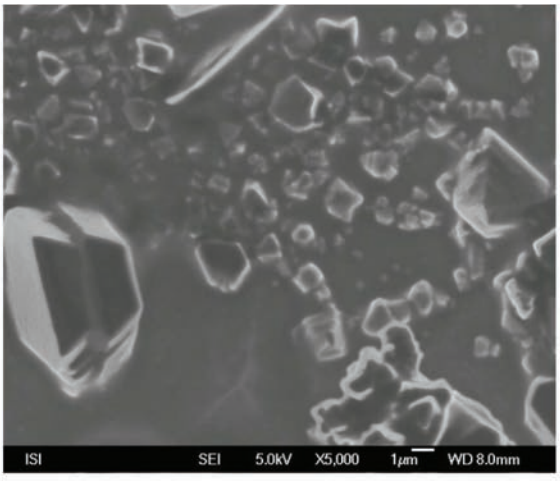



Fig. 12.

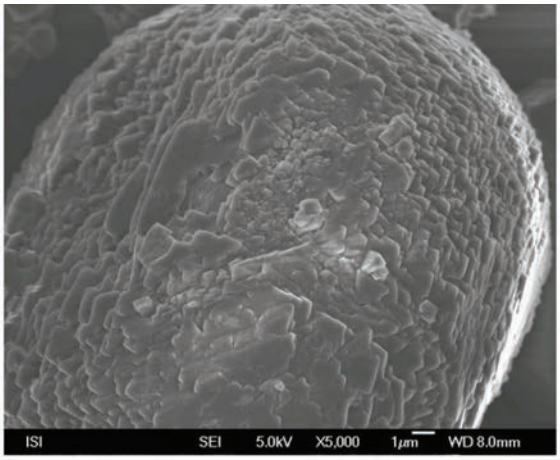



Fig. 13.

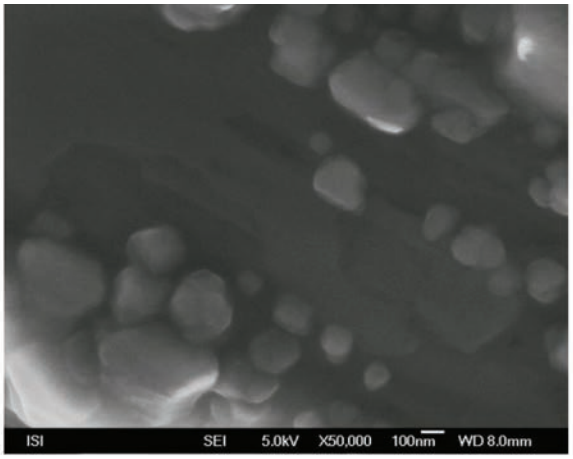



Fig. 14.

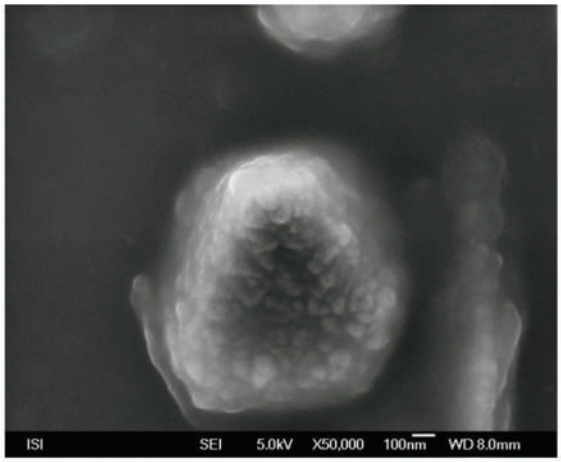



Fig. 15.

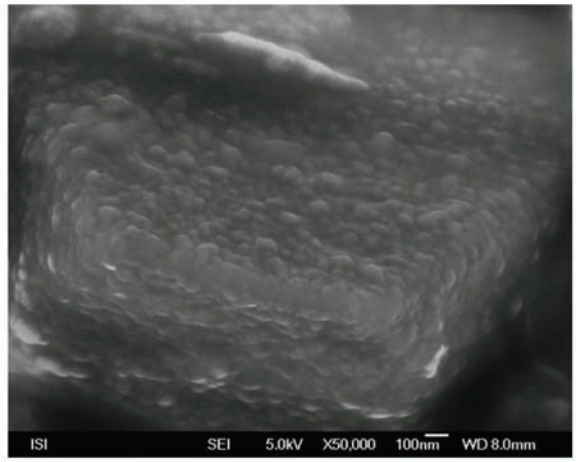



Fig. 16.

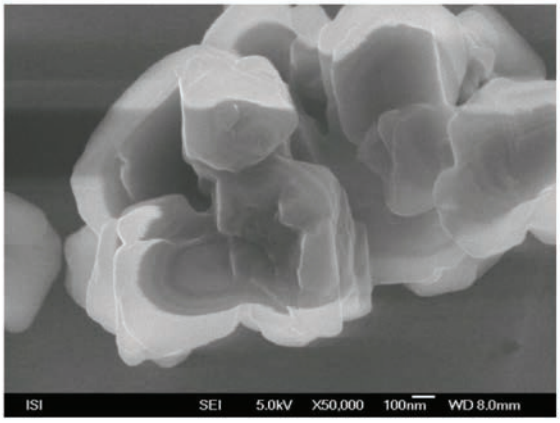



Fig. 17.

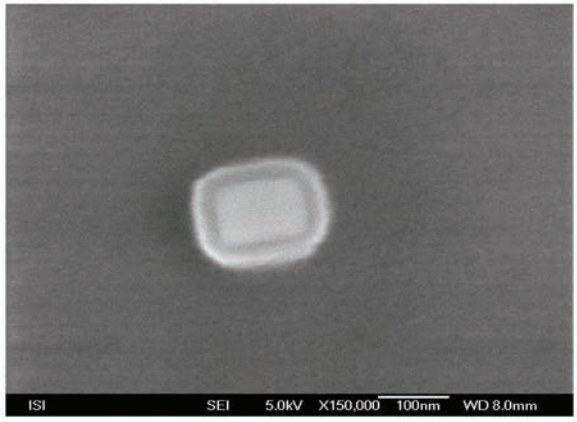



Fig. 18.

All fullerene C 60 samples exhibited the above mentioned nanoporous structure. Also interesting is the presence of cubic, probably diamond structure (Fig. 18).

The observed structural characteristics of the studied sample of non-substituted fullerene C 60 sample are in good agreement with the above theoretical considerations of its probable microstructure and found sorption properties for toluene vapors. Further study of the microstructure of gamma irradiated base and its amino and chlorine derivatives may either confirm or refute these first considerations.

## 3. Conclusions

The microstructure of the studied fullerene C 60 sample, before and after recrystallization, is likely to consist of regularly arranged layers of single or agglomerated C 60 molecules, mainly crystallizing hexagonally. As a result of this arrangement, the microporousity is also found, which is rather recrystallized by the sample.

From the results presented in this article, the continuation of research focused on the use of carbon structures based on fullerene C 60 has its significance and potential in the future development of further use of sensors and sensor technologies. Research will be carried out in connection with the study of the possibility of applying a specially prepared detection layer to the active layer of the QCM sensor and then test its universal use, decontamination, repeatability, etc. A very important step in further research will be to study its response to very low concentrations of both chemical warfare agents and industrial chemicals after its permeation by barrier polymeric and sorption materials.

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