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STRUCTURAL CHARACTERIZATION OF NANOMATERIALS

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Abstract

Sol-gel method opens new possibilities for synthesis of nanomaterials with application in biotechnology and medicine as matrices for immobilization of cells, enzymes and other biomolecules. The main purpose of the present work is to study of the sol-gel synthesis and the structure of silica hybrid nanomaterials containing different quantities of organic component. FT-IR spectra show that in hybrids synthesized by ETMS or MTES strong chemical bonds are observed. The average size of nanoparticles on the sample surface is about 20 - 50 nm and formation of self-organized structures is observed.

Keywords: *sol-gel synthesis, nanomaterials, self-organization.*

Introduction

Inorganic/organic nanomaterials are a remarkable family of amorphous nanocomposite materials, which have been studied extensively for application in biotechnology, medicine, dentistry and other different areas [1, 2]. The material properties as thermal and electrical conductivity, mechanical strength, flexibility, optical density, corrosion resistance can be widely controlled by adjusting composition, nanophase size, and chemical bonds between organic and inorganic parts [3, 4].

The development of hybrid functional nanocomposites that incorporate organic polymers and inorganic components is a recent trend in materials synthesis. Different organic materials, such as gelatin, alginic acid, PEG, PVA, PAAG, AA, agar and others are included In their structure. The hybrid is formed in situ in a polymer solution by self-assembling of sol particles generated in the course of hydrolysis of the metal-organic precursors. [5-9]

In this work, polyethylene oxide (PEO) was chosen as an organic polymer because it is a cheap commercially available aliphatic polyether which can be linear or branched and in a broad range of molecular masses from less than a few hundred to several millions. Another important feature of PEO is its solubility in water and alcohols. Furthermore, PEO is characterized by hydroxyl groups, which can be used to obtain oligomers able to react with sol-gel reactants such as metal alkoxides [10-14].

The present study deals with preparation, structural characterization of hybrid nanomaterials based on different type of inorganic metal alkoxide as tetraethylortosilicate (TEOS); tetramethylortosilicate (TMOS); methyltriethoxysilane (MTES); ethyltrimethoxysilane (ETMS) and different quantity PEO.

Materials and Methods

Nanocomposite hybrid materials were prepared by the sol-gel method at room temperature and strictly controlled pH conditions. Four types of inorganic precursors: tetraethylortosilicate (TEOS); tetramethylortosilicate (TMOS); methyltriethoxysilane (MTES); ethyltrimethoxysilane (ETMS) and the organic compound polyethylene oxide (PEO) were used for synthesis of nanomaterials. In all the cases the ratio Precursor/H_2O is kept constant and equal to 1. A small amount of 0.1 M HCl is introduced to increase hydrolysis rate (pH~1.5) and phosphate buffer with pH=7.00 ± 0.02 at 20^0C. In the process of synthesis of hybrid materials 20% percent of the silica precursors were replaced with organic component.

For studying the structure of synthesized hybrids the following methods have been used: FT-IR (IR-MATSON 7000–FTIR spectrometer), XRD (X-ray PW1730/10 diffractometer, in the 2θ range of 50–800, Cu-Kα radiation), EDS (RONTEC EDS System), SEM (Philips-515) and AFM (NanoScope Tapping Mode ^{TM}).

Results and Discussion

The results from the XRD-analysis (Fig.1) prove that all the studied hybrids have an amorphous structure, which is in good correlation with the studies of Lana and Seddon [15]. At the same time the type of the XRD pattern indicates that some processes of ordering take place.

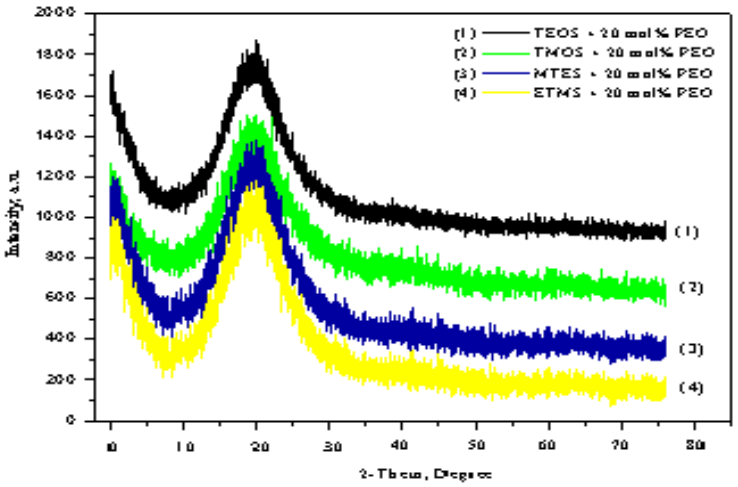

Fig.1. XRD patterns of nanomaterials containing PEO

The FT-IR spectra of synthesized inorganic-organic materials (Fig.2) show that in all samples bands at 1080 cm^{-1}, 790 cm^{-1} and 480 cm^{-1} are observed. They are assigned to ν_{as}, ν_s and δ of Si-O-Si vibrations, but at the same time the band at 1080 cm^{-1} can be related to the presence of Si-O-C, C-O-C and Si-C bonds. The band at 960 cm^{-1} is due to a stretching Si-OH vibration. The band at 1439 cm^{-1} is assigned to C-O-H vibrations. The characteristic bands at around 3450 cm^{-1} and at 1620 cm^{-1} assigned to H-O-H vibration can also be detected. These bonds in the samples with MTES and ETMS are in narrower range. The absorption band at 2975 cm^{-1}, 1255 cm^{-1}, 880 cm^{-1}, 694 cm^{-1}, due to the presence of Si-O-R (CH_3 and C_2H_5) and

Si-C bonds have been observed. This fact directly proves the presence of strong chemical bonds between inorganic and organic parts of nanomaterials with MTES and ETMS.

From the data of BET analysis it has been established that the surface area is in the range from 520 to 260 m^2/g dependence on silica sources. The results showed that the surface area depends on the type of precursor. The obtained results can be applied as carriers for cell immobilization.

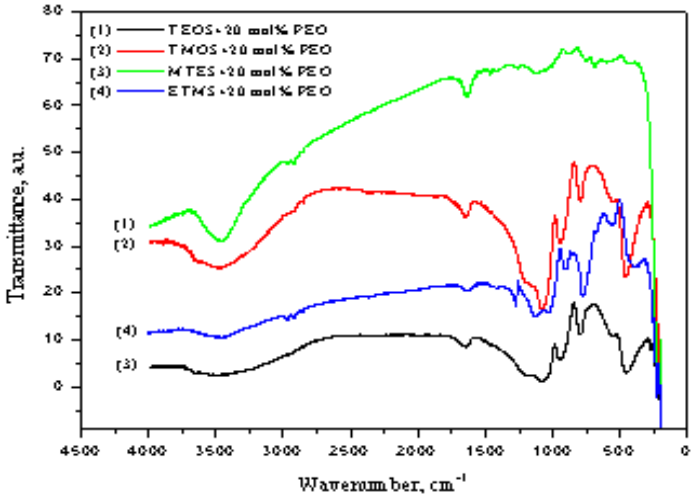

Fig.2. FT-IR-spectra of silica nanomaterials

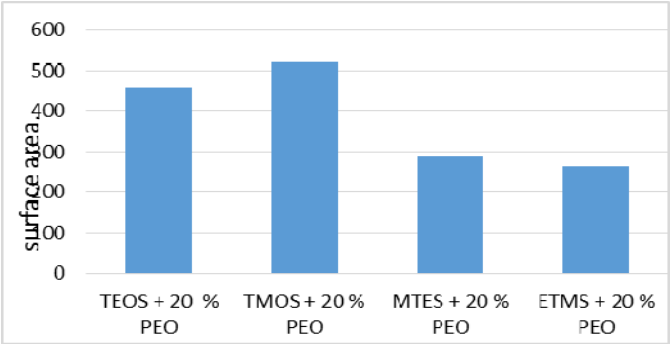

Fig.3. BET analysis of silica nanomaterials

However more detailed information on the nanostructure of the matrices is obtained from the SEM and AFM studies (Figs. 4-7). A very good agreement between SEM and AFM data of synthesized hybrid materials is found. In the case of MTES+20 % PEO the SEM study shows the presence of microaggregates dispersed in flat and relatively homogeneous matrix. This type of variation of microstructure is confirmed by the AFM images (Figs.4, 6). The observed nanoscaled formations could be assigned to the surface structure of the particles building the aggregates registrated by SEM.

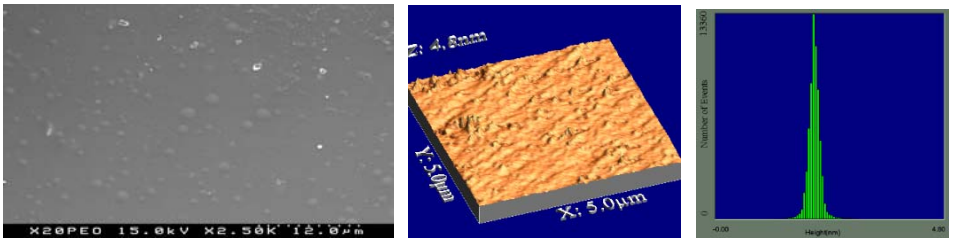

Fig.4. SEM, AFM image and roughness analysis of the hybrids with TEOS containing 20 % PEO

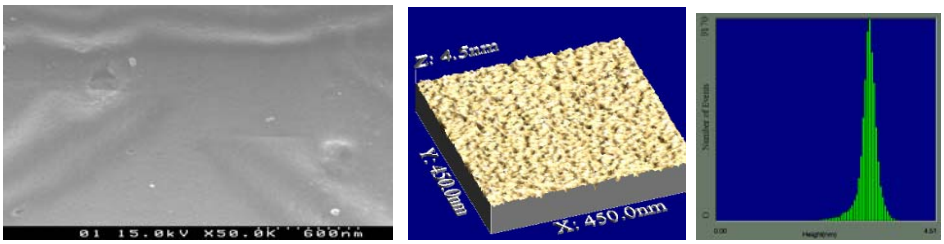

Fig.5. SEM, AFM image and roughness analysis of the hybrids with TMOS containing 20 % PEO

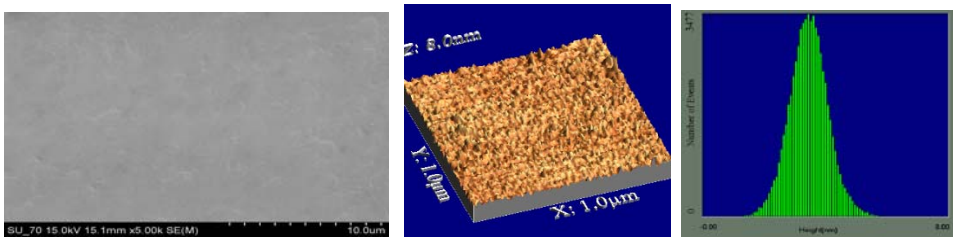

Fig.6. SEM, AFM image and roughness analysis of the hybrids with MTES containing 20 % PEO

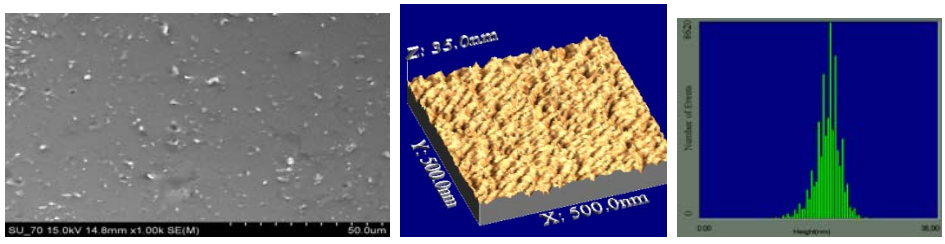

Fig.7. SEM, AFM image and roughness analysis of the hybrids with MTES containing 20% PEO

The results of the both studies givecomplete information about the evolution processes of the self-organizing structures of synthesized materials. Complete coincidence between the sizes of nanoparticles (about 20-50 nm) determined by SEM and AFM is observed. In the AFM image the nanostructural evolution is also well presented.

Conclusion

Inorganic-organic silica hybrid amorphous nanomaterials containing PEO are obtained via sol-gel method at room temperature. Self-organized nanostructures have been observed by AFM and the size of nanoparticles is from 20-50 nm. IR investigations show strong chemical bonds between inorganic and organic parts in the synthesized materials. The presence of an hybrid nanostructure with well-defined nanounits with spherical geometry and their aggregates, formed by self-organizing processes, is clearly observed by AFM studies. The surface morphology and structure of nanobuilding blocks in each synthesized hybrid is different and dependeds on its chemical composition.

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