Silica hybrid nanocomposites

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Abstract: In this work we present experimental results about the formation, properties and structure of sol – gel silica based biocomposite containing Calcium alginate as an organic compound. Two different types of silicon precursors have been used in the synthesis: tetramethylortosilicate (TMOS) and ethyltrimethoxysilane (ETMS). The samples have been prepared at room temperature. The hybrids have been synthesized by replacing different quantitis of the inorganic precursor with alginate. The structure of the obtained hybrid materials has been studied by XRD, IR Spectroscopy, EDS, BET and AFM. The results proved that all samples are amorphous possessing a surface area from 70 to 290 m²/g. It has also been established by FT IR spectra that the hybrids containing TMOS display Van der Walls and Hydrogen bonding or electrostatic interactions between the organic and inorganic components. Strong chemical bonds between the inorganic and organic components in the samples with ETMS are present. A self-organized nanostructure has been observed by AFM. In the obtained hybrids the nanobuilding blocks average in size at about 8 – 14 nm for the particles.

Keywords: Sol gel, silica hybrid nanocomposite, self-organizing

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1 Introduction

The investigation of inorganic – organic hybrid materials, synthesized by the sol-gel method with an organic phase dispersed on a nano level in the inorganic matrix, has gained widespread attention in the recent years. The sol-gel process is used to form nano-scale hybrid materials. It is supposed that interaction between phases in the hybrid materials, where the inorganic phase is often covalently bonded with the organic polymer, will lead to more valuable properties compared to classical composites. Hybrids are formed in situ by hydrolysis and condensation of metal alkoxides and various combinations of polymers to create a nanoscale mixture of inorganic-oxides and organic polymers by the sol-gel method [1–7].

The organic phase has also been used as a templating component for the nanoporous inorganic oxides. Indeed, nanostructured materials with well-defined pore size (2–50 nm) are well known and can be prepared via self-assembly of surfactants and inorganic metal oxides [8–15].

The organic makeup of the hybrid material can improve the adhesion between the coating and a polymer substrate, and the inorganic part can increase the hardness of the coating.

The most frequently used organic components in the hybrid materials synthesis are polyethylene glycol (PEG), polyvinyl alcohol (PVA), acryl amide (AA), polyethylene oxide (PEO) and others [16–19].

The hybrid nanocomposite materials prepared with the help of sol-gel chemistry have been applied to different research fields for years. One of the fastest growing research directions in the field of sol-gel science and technology is the immobilization of various biomolecules in sol-gel matrices retaining their bioactivity. A number of enzymes, antibodies and cells have been successfully immobilized in silica and organic-inorganic materials [17–27]. The porous structure of the hybrids is a major parameter for the efficiency of the immobilization process as the pores of the hybrid materials having nano dimensions helping the diffusion of the substrates and products of the enzyme reaction.

Microencapsulation of biomolecules and living cells in Calcium alginate gel beads coated with a semipermeable membrane have been widely investigated for industrial, pharmaceutical and medical applications. The main function of core materials is to entrap biomolecules and living cells rapidly whilst maintaining their biological activity [24–28].

In some work the silica hybrids containing Calcium alginate have been synthesized by the sol-gel method. The hybrids are made from two kinds of silicon alkoxide precursors, tetramethoxysilane and 3-aminopropyltrimethoxysilane [28–32].

In our previous works we have compared pure silica matrices with organic-inorganic hybrid matrices obtained by using different inorganic precursor (TEOS, TMOS, ETMS, MTES) and organic compound such as: agar-agar, polyacrylamide gel (PAAG), PEG, PVA and AA [33–38].

The purpose of the present work is to synthesize and investigate the influence of
the inorganic precursors, TMOS and ETMS, on the synthesis and structure of hybrid materials containing Calcium alginate.

2 Experimental

Sol - gel transparent silica and hybrid matrices with varying quantities of organic compounds have been synthesized at room temperature and controlled pH conditions pH∼1.5 and pH=7. (Fig. 1) The inorganic-organic hybrid materials have been prepared by substituting part of the inorganic precursor with alginate (5, 10, and 15 mol %). Two types of silicon alcoxide precursors have been used: tetramethylortosilicate (TMOS) and ethyltrimethoxysilane (ETMS) purchased from “Merck”. A poly-step sol-gel procedure is used at strictly controlled conditions in order to obtain the desired nanostructured materials. In all cases the ratio TMOS/H$_2$O is kept constant and equal to 1. No alcohol is added as a co solvent. A small amount of 0.1 N HCl is introduced to increase the rate of hydrolysis (pH∼1.5) and phosphate buffer with pH=7.00±0.02 at 20 °C is used for pH adjustment. To synthesize the organic component (Ca alginate) the following chemicals have been used: alginic acid, potassium calcium chloride and NaOH.

No phase separation is observed before and after the gelation point. The gelation time of samples is from several minutes to several hours depending on the type of the precursor. The addition of the organic component leads to a faster polymerization. Thin transparent hybrid flakes are obtained using TMOS as a precursor in hybrid synthesis, when using ETMS as a precursor the obtained thin films possesses a good adhesion toward the glass surface. The drying procedure is carried out at room temperature.

For structure investigation of the synthesized hybrids the following methods have been used: XRD (X-ray PW1730/10 diffractometer, in the 2θ range of 50–800, Cu-Kα radiation), FT-IR (IR- MATSON 7000–FTIR spectrometer), Surface Area Analysers (BET-Analysis - Gemini 2370 V5.00), Energy Depressives System (EDS –Rontec EDS System) and Atomic Force Microscopy (AFM - NanoScope Tapping Mode$^{TM}$).

3 Results and discussion

The results from the XRD - analysis prove that all the studied hybrids have an amorphous structure (Fig. 2, 3). Using TMOS as a precursor, the intensity of the amorphous halo decrease compared to thoese when ETMS was included. The results show that with an increase in concentration of calcium alginate the intensity of the curves decreases.

The FT-IR spectra of synthesized inorganic-organic materials are shown in Figures 4 and 5. The bands at 1080 cm$^{-1}$, 790 cm$^{-1}$ and 480 cm$^{-1}$ are observed in the IR spectra of all studied samples. They are assigned to $\nu_{as}$, $\nu_s$ and $\delta$ of Si-O-Si vibrations, but at the same time these bands 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 bands at 1439 cm$^{-1}$ is assigned to C-O-H vibrations. The characteristic bands at around 3450 cm$^{-1}$ and at 1640 cm$^{-1}$ assigned to H-O-H vibration can also be detected.
In the samples synthesized by ETMS the absorption band at 2975 cm$^{-1}$, 1255 cm$^{-1}$, 880 cm$^{-1}$ and 694 cm$^{-1}$, due to the presence of Si-O-R (CH$_3$ and C$_2$H$_5$) and Si-C bonds
have been observed. This data directly proves the presence of strong chemical bonds between the inorganic and organic components of these hybrid materials.

The chemical content in the samples has been determined by Energy Depressives System (EDS). The presence of Si, O, N, Na, P, S, Cl and K has been detected.

From the data of BET analysis it has been established that the surface area is in the
Fig. 5 FT-IR-spectra silica nanocomposite hybrid (ETMS) containing different quantity Calcium alginate. The results clearly show that with increasing the percentage of the organic component, the surface area decreases.

Fig. 6 AFM images of silica (TMOS) hybrids containing 5 mol % calcium alginate. A self-organized nanostructure has been observed by AFM. In the obtained hybrids the nanobuilding blocks are made up of nanounits of SiOx groups and that Van der Walls and Hydrogen bonding or electrostatic interactions between the nano-building blocks exist. In the samples synthesized with TMOS and ETMS the average size of nanoparticles of
Fig. 7 AFM images of silica (TMOS) hybrids containing 15 mol % calcium alginate.

Fig. 8 AFM images of silica (ETMS) hybrids containing 5 mol % calcium alginate.

the surface is about 8 - 14 nm and the dimensions of their aggregates are about 20 – 80 nm (Fig. 6 – 9).

4 Application

The synthesized hybrids have been tested as carriers for thermostable cell adsorption. For the cells of interest maintaining their vitality and preserving their biosynthetic functionality is key. The obtained biocatalysts are applied in the biodegradation processes of the toxic substance 4 – cyanopyridine.

The effect of the addition of an organic component to the pure silica matrices was estimated. It can be clearly seen that the inclusion of Calcium alginate favors the increase
of enzyme activity, especially upon re-use. The change in percentage of the organic component also influences immobilization efficiency. As in our previous work, a 5 % composition appeared to be the most suitable. Including ETMS as an inorganic precursor leads to better results with respect to operational stability. At the 8th reaction cycle the enzyme retained 41 % activity, where the activity of the first cycle was assumed as 100 %. Cell loading was 13 % from the total quantity of cells used for immobilization 100mg (13 mg/g carrier) and cells are free to react with the substrate (4- cyanopyridine) and the enzyme – substrate reaction is accomplished without mass transfer limitations. From these experiments it has been shown that the synthesized hybrid nanomaterials were successfully applied for cell immobilization, where they had a favourable effect on cell vitality and enzyme stability and could be used for 8 reaction cycles of 4 – cyanopyridine degradation with a reduced loss of activity.

All results concerning cell immobilization in hybrid matrices were performed by the research group of Prof. E. Dobreva with the participation of PhD student L. Kabaivanova (Institute of Microbiology, Sofia, Bulgarian Academy of Sciences).

5 Conclusion

Inorganic-organic silica hybrid transparent materials, containing Calcium alginate, are obtained via the sol-gel method at room temperature. All the studied noncomposite hybrids have an amorphous structure. At the same time the sharpening of the amorphous halo indicates that some processes of ordering are carried out.

The surface area in all samples is in the range of 70 to 290 m²/g . With IR, the inorganic and organic components were found to interact by Van der Walls forces, hydrogen bonding or electrostatic forces in the synthesized hybrids with TMOS. In the synthesized hybrids with ETM, IR has also demonstrated strong chemical bonds to exist between the organic and inorganic components. Self-organized nanostructures have been observed by AFM and the average size of the nanoparticles is about 8 – 14 nanometers and the
dimensions of their aggregates are about 20 – 80 nm.

Cell immobilization experiments showed that the synthesized hybrid nanomaterials were successfully applied in maintaining cell vitality and enzyme stability for 8 reaction cycles of 4-cyanopyridine degradation where on the 8th cycle, 41% of enzyme activity was sustained.

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