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# SYNTHESIS OF HIGH FLUORESCENT SILICA HYBRID MATERIALS BY IMMOBILIZATION OF ORANGE PEEL EXTRACT IN SILICA-SILSESQUIOXANE MATRIX

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## SYNTHESIS OF HIGH FLUORESCENT SILICA HYBRID MATERIALS BY IMMOBILIZATION OF ORANGE PEEL EXTRACT IN SILICA-SILSESQUIOXANE MATRIX

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Sol-gel chemistry has been easily modified to the changing needs of society to produce fine-tuned sol-gel nanostructured materials for relevant applications. In this respect, there is an increasing need for natural and versatile raw materials, as well as biocompatible compounds that could be extensively used as biomarkers for bioimaging in diagnostic or therapy. Silica-based materials are widely used in the field of biomedicine due to their chemical inertness and biocompatibility.

In the present paper, an orange peel extract was immobilized inside inorganic silica and hybrid silica-silsesquioxane polymeric networks. Silica and organo-modified silica matrices have been synthesized through a templated sol-gel route of TEOS and an organosilsesquioxane (octaisobutyltetracyclo[7.3.3.1<sup>5,11</sup>] octasiloxane-endo-3,7-diol), with D-glucose as template, and for comparisons a non-ionic surfactant (tetraethylene glycol monohexadecyl ether) has been also used. The bioactive principles contained in the molecules from orange peel extract were preserved after immobilization in both silica and silica-silsesquioxane networks. Moreover, the fluorescence properties were amplified by more than 10-20 times than native orange peel extract. The structural properties of final materials have been studied by FT-IR, UV-VIS-NIR and fluorescence spectroscopy. Dynamic Light Scattering measurements and transmission electronic microscopy were used in order to estimate the size and morphology of hybrid materials with orange peel extract immobilized in silica networks.

**Keywords:** orange peel extract, immobilization, sol-gel process, silsesquioxane

## 1. INTRODUCTION

Silicon and siliceous compounds such as silica have been understood to play an active role in organism health and development [1]. Beside these silicon compounds, there are many researches conducted in the last years that generated a growing interest in the potentially important role of flavonoids in maintaining human health.

Among the natural extracts with benefic activities that may be valorized in the biomedical field, orange peel extract (OPE) is a rich source of flavonoids, being a mixture of polymethoxyflavones high bio-active (as major constituents), compounds associated with antioxidant, anti-inflammatory, antitumor activities and with potential chemopreventive properties [2, 3]. Unlike many phytochemicals, orange peel extract is a soluble lipid, a property which is desirable in many drug products since facilitate passage across biological membranes, and thus the bioavailability are enhanced. Orange peel and its extracts have been used in a variety of herbal drug products in combination with many different plant components and extracts [4]. These naturally bio-active compounds present in plants such as flavonoids, phenolic compounds, terpenes and many others are believed to exhibit disease preventive properties. Diets containing some of these substances have been shown to be protective against diseases such as colon and breast cancer in animals [5-7]. For example, a recent invention relates the beneficial effects of orange peel extract, by providing of some compositions and methods of inhibiting tumor cell growth and treating and preventing cancer based on administration of an orange peel extract either alone or in combination with other phytochemicals [8]. A similar study presents a method for preparation of some plant extract powder and oral compositions containing plant extract porous powder carrier having activities of prevention and treatment for periodontal diseases or tooth decay preventing effect [9]. A first encapsulation method for some essential oils (among them orange peel extract), used microbial microcapsules that contain one or more fungal, bactericidal and algal cells as encapsulating matrix [10].

The purpose of this research is to expand the bioencapsulation process used for entrapping of organic biomolecules (enzyme, proteins, nucleic acids, cells etc) in different matrices, towards an immobilization method of organic molecules from a natural extract (orange peel extract) inside hybrid silica host matrices which present high stability to temperature and other environmental factors and have the required characteristics for enhancing of some specific optical properties of natural extract – fluorescence. This process which involves the use of hybrid

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3 organo-siloxanes compounds is similar to mineralization processes from living organisms (bio-  
4 mineralization occurs in mild conditions, in which proteins and cells are active: room  
5 temperature, neutral pH etc.). Moreover, the process represents an adequate method for synthesis  
6 of highly fluorescent silica hybrid materials, a direct result being the amplification of  
7 fluorescence properties as comparing to those of native orange peel extract.  
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12 Silicate and derivative silicate frameworks are the most abundant compounds in nature.  
13 Their use in science, medicine and engineering has increased drastically in the last decade [1].  
14 Silica-based materials are widely used in the field of biomedicine due to their multiple  
15 advantages such as: biocompatibility, excellent photonic media as a result of their low optical  
16 losses, good mechanical properties, chemical, photochemical and thermal stability and long-term  
17 environmental stability; they are not a food source for microorganisms.  
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22 Oligomeric silsesquioxane (POSS) – a class of three-dimensional organosiliceous  
23 compounds, due to their octahedral structure, nanometer size, as well as good optical properties,  
24 represent potentially nanoconstruction sites very useful for obtaining of hybrid-host matrices for  
25 sensitive natural extracts. In this respect, in the present paper a new class of templated host  
26 matrix of silica – silsesquioxane type was used, appropriate for entrapping of orange peel extract  
27 at room temperature, by using raw materials that are not hazardous for human health or  
28 environment. The silsesquioxane molecule combines a truly hybrid (inorganic – organic)  
29 architecture, which contains an inner inorganic framework made up of silicone and oxygen that  
30 is surrounded by organic substituents. The organic groups are attached on the surface of silica  
31 matrix through the non-hydrolysable Si – C bonds and functions as the network modifier [11]. In  
32 addition, the caged nanostructures (with typical size of 1-3 nm), have been thought as the  
33 smallest possible particles of silica [12]. Another characteristic of this compound is its chemical  
34 composition: being a hybrid  $(\text{RSiO}_{1.5})_n$ , intermediate between silica ( $\text{SiO}_2$ ) and silicon ( $\text{R}_2\text{SiO}$ )  
35 (fig. 1), this leads to a thermally and chemically robust matrix [13].  
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48 The molecule of such a silsesquioxane derivate presents reactive functionalities like OH  
49 groups adequate for polymerization, formation of hydrogen bonds or polymeric graphing  
50 towards branching polymeric chains and nonreactive organic functionalities, R for solubilization  
51 and compatibilisation [14]. Thus, the entire silsesquioxanic molecule confers a precise three-  
52 dimensional structure, the nanostructured units may be easily incorporated into common  
53 polymeric materials via copolymerization, grafting or blending [15]. The incorporation of POSS  
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3 derivatives into polymeric materials can lead to significant improvements in polymer properties  
4 which include increases in use temperature, oxidation resistance, surface hardening and  
5 improved mechanical properties [11]. Applications of silsesquioxanes utilized the cage structures  
6 to act in several roles, including catalysts [16], metal complexes [17, 18], carriers for drug  
7 delivery process [19], encapsulation material for communications, optoelectronics [20] and also  
8 to synthesize new porous materials [21, 22]. Their potential to mimic silica surfaces arises from  
9 the similarity of silsesquioxanes to siliceous clusters that possess the structural and electronic  
10 features of hydroxylated silica surfaces. Most of the researches on these compounds have been  
11 conducted towards the development of polymer-inorganic nanocomposites with properties  
12 focusing on materials science. Possible uses in biotechnology and medicine have received only a  
13 partial emphasis as compared to applications in engineering and materials science. Therefore, it  
14 is interesting to evaluate the suitability of new silica-silsesquioxane hybrid networks - as host  
15 matrices used for orange peel extract immobilization in order to investigate the role of  
16 silsesquioxane compound as building blocks in sol-gel immobilization process and how these  
17 matrices may preserve and even enhance some of specific optical properties of orange peel  
18 extract such as fluorescence properties.  
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## 32 **2. EXPERIMENTAL**

### 33 **2.1. Materials and preparation method**

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36 Chemicals were purchased from commercial sources (Fluka, Merck):  
37 tetraethylorthosilicat (TEOS), Octaisobutyltetracyclo[7.3.3.1<sup>5,11</sup>]octasiloxane-endo-3,7-diol (Sq),  
38 tetraethylene glycol monohexadecyl ether (PEG), D-glucose (Gl), ethanol. The natural extract  
39 (orange peel extract – OPE) was obtained from cold-pressed peel oil solids of orange fruits. The  
40 peel oil solids were dissolved in warm ethanol and after several repeated washes a yellow oil  
41 product with a reproducible amount of flavonoids is obtained. The extract contains a mixture of  
42 various homologs of methylated flavonoids.  
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49 For the study of orange peel extract (OPE) immobilization, a silica pre-hydrolysed sol  
50 was initially prepared in an acidic catalysis (pH ~ 3) using a standard protocol: a molar ratio of  
51 TEOS:H<sub>2</sub>O:Et-OH = 1:2:4. The resulted mixture was stirred for two hours at 60-62°C. In order to  
52 obtain a templated sol, the reaction mixture was cooled and neutralized (~30°C, pH ~6) and a  
53 template solution was added to the sol (an aqueous solution of 2M D-glucose for obtaining D-  
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glucose templated sol and 0.8 M tetraethylene glycol monohexadecyl ether, for PEG templated  
sol). After one hour of stirring with template compound, the templated sols thus obtained were  
used for orange peel extract immobilisation step. A part from this templated sol was kept as  
reference material. 1 mL orange peel extract (prepared by dissolving 0.1050g extract in 2 mL  
water) and 6 mL alcoholic solution 0.0053 M octaisobutyltetracyclo[7.3.3.1<sup>5,11</sup>]octasiloxane-  
*endo*-3,7-diol were mixed at room temperature for one hour, under magnetic stirring. This  
mixture of natural extract and silsesquioxane was dropping added in 12g of two templated sols  
(with PEG and D-Glucose), in order to realize the OPE entrapment inside a silica-Sq hybrid  
matrix; thus OPE-PEG-SiO<sub>2</sub>-Sq and OPE-Glucose-SiO<sub>2</sub>-Sq systems were obtained. For  
comparison purpose, 1 mL orange peel extract solution (previously prepared) was added in other  
10g of two templated sol, in order to realize the immobilisation in inorganic silica matrix; OPE-  
PEG-SiO<sub>2</sub> and OPE-Glucose-SiO<sub>2</sub> systems were obtained. All four systems were then sealed  
with a parafilm (with holes that allow the evaporation of solvent and reaction by-products) and  
kept 12 h at room temperature under magnetic stirring. After this period, the aging step was  
achieved by placing the samples in an oven and kept three days at 35°C. Then, the yellow glass  
silica polymeric materials (named as OPE-PEG-SiO<sub>2</sub>-Sq, OPE-PEG-SiO<sub>2</sub>, OPE-Glucose-SiO<sub>2</sub>  
and OPE-Glucose-SiO<sub>2</sub>-Sq) were grinded into fine powders and stored at room temperature for  
subsequent characterizations.

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**2.2. Methods and equipment.** UV-VIS-NIR spectroscopy was used for structural  
analysis of flavonoids; the electronic spectra were recorded between 200 and 1850 nm using a  
Jasco double – beam V570 Spectrophotometer. The structures of the immobilized flavonoids  
from orange peel extract were studied by FT-IR spectroscopy and were recorded between 4000 –  
400 cm<sup>-1</sup> by Jasco 620 FT-IR. Fluorescence measurements were carried out with a FP-650  
Spectrofluorimeter, Jasco, equipped with a microcomputer for data recording. The samples were  
illuminated with a 260 nm excitation light and the fluorescence emission was collected at 305  
nm. Fluorescence assays were performed on solid samples of native extract and immobilised  
extract in the inorganic silica and hybrid silica-silsesquioxane networks. The hydrodynamic  
diameters of immobilized extract silica powders suspended in ethanol were measured by  
dynamic light scattering (DLS) and were performed with a Zetasizer Nano ZS from Malvern  
Instruments. The size and morphology of polymeric aggregates with entrapped orange peel  
extract were investigated by transmission electron microscopy (TEM), Philips, 208 S.

### 3. RESULTS AND DISCUSSION

The organic-inorganic hybrid materials may be prepared in various ways. The simplest method relies on dissolution of organic molecules in a liquid sol-gel [23]. The other way uses the impregnation of a porous gel in the organic solution [24]. In the third type, the inorganic precursor either already has an organic group or reactions occur in a liquid solution to form chemical bonds in the hybrid gel [25]. The sol-gel reaction of metal alkoxide is one of the most effective methods for the preparation of hybrid materials because of the low reaction temperature [21]. Here we report the incorporation of an octameric silsesquioxane monomer incompletely condensed in a classical oligomeric sol originated from sol-gel processing, by simply mixing of monomeric silsesquioxane with a templated pre-hydrolyzed sol of TEOS, followed by copolymerization reactions. The matrices obtained were used for orange peel extract immobilization in two silica networks: a hybrid silica-silsesquioxane network, and as reference matrix – an inorganic silica network. This process involved two main steps:

- I. The pre-forming of templated silica sols, using the acid-catalyzed hydrolysis and condensation of tetraethylorthosilicate (TEOS) in presence of D-Glucose template and for comparing with PEG template (tetraethylenglicol mono-hexadecylether).
- II. The immobilization of orange peel extract into inorganic silica and hybrid silica-silsesquioxane networks. In order to realize the immobilization inside a hybrid silica-silsesquioxane network, the silsesquioxanic precursor (nanobuilding block, octaisobutyltetracyclo [7.3.3.1<sup>5,11</sup>] octasiloxan-*endo*-3,7-diol) was added together with natural extract in prepared templated silica sol.

Silica has no crystalline properties, but constitutes a framework of tetrahedral coordinated Si–O–Si bonds in which many vertices are ended with OH groups. Colloidal silica surfaces have been shown to form strong hydrogen bonds [1]. These terminal hydroxyl groups involved in hydrogen bonding lead to formation of a pseudo-crystalline cluster of silica. Furthermore, by including the silsesquioxane monomers with rigid inorganic cores, flexible organic substituents and OH groups useful not only as polymerizable groups for copolymerization reactions, but also for involving in hydrogen bonding, an appropriate matrix with good performance for physical interactions with the functional groups from natural extract is obtained. The natural extract immobilization in such polymeric networks assures an optimal conformational arrangement. The



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3 steric constraints inhibit the mobility leading to the immobilization of organic molecules from  
4 natural extract in a conformational arrangement favorable for transmission of fluorescence  
5 properties by achievement of some weak interactions (hydrogen bond,  $\pi$  electrons extended  
6 conjugation, donor-acceptor interactions). Thus, the organic molecules were captured in sol-gel-  
7 oxidic network. In this mode the weak extract – matrix interactions which appear between free  
8 OH groups of polymeric matrix and carbonyl and hydroxyl groups of flavonoidic and  
9 polyhydroxilic compounds from natural extract, allow their adsorption on microporous surface of  
10 matrix, thus enhancing the thermal stability of immobilized extracts, without affecting the  
11 specific properties as occurs in the case of some strong chemical bonds. It is evident that a  
12 chemical bond of natural extract with polymeric matrices may lead to the inactivation of  
13 flavonoidic molecules losing thus their fluorescence properties.

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23 D-glucose is an atypical template that may fulfil the role of a conventional directing agent  
24 by virtue of its highly polar functional groups which permit the formation of some collectivity  
25 (known as aggregates or glucidic assemblies) that may physically retain the organic molecules.  
26 This glucidic template does not form an ordered structure (with uniform pores) as usual  
27 templates, but this disordered structure of glucidic assemblies is sometimes advantageous due to  
28 the fact that it allows the spreading of properties along all directions. The organic flavonoid  
29 molecules are bound to the sites of the sugar layer by non-covalent interactions, such as  
30 hydrogen bonds and Van der Waals interactions. These glucidic molecules can favorize the sol-  
31 gel reaction by hydrogen bond formation between molecules or glucidic aggregates and silicate  
32 intermediate species, thus determining the increase of gelation time.

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41 By using this immobilization process, a homogeneous and stable distribution of  
42 silsesquioxane building blocks in final materials is achieved, without separation of some undesired  
43 microphases. In the polymer hybrids described above, hydrogen bonding interactions between  
44 residual silanol groups and carbonyl and hydroxyl groups of flavonoid compounds from orange peel  
45 extract were confirmed by UV-VIS and FT-IR spectroscopy. We consider that such hydrogen  
46 bonding interactions were strong enough to permanently integrate the natural extract as an integral  
47 component of inorganic silica and hybrid silica modified with silsesquioxane networks.

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By comparing the maximum absorption bands characteristic for flavonoidic compounds  
which appear in orange peel spectrum, with those of immobilized extract samples in different

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4 inorganic silica and hybrid silica-silsesquioxane networks, the following observations can be  
5 made (Fig. 2):  
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- 7 • both absorption bands at 256 nm and 316 nm existent in orange peel extract and assigned to  
8  $n \rightarrow \pi^*$  transitions of auxochrom and chromophor groups of OH, COOH and C = O type  
9 from aromatic flavonoidic structure, are shifted towards higher wavelengths (284 nm/280 nm  
10 and 332 nm respectively, *bathocrom* effect), in the electronic spectra of immobilized extract  
11 samples with PEG and D-glucose templates (Fig. 2A' and B');  
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- 13 • in NIR domain, the orange peel extract present two distinct regions at 1460-1560 nm and  
14 1700–1750 nm, characteristic for free and associated OH groups. The first absorption region  
15 appears in immobilized extract samples as a broad band shifted towards lower wavelengths:  
16 1420–1460 nm for samples obtained with tetraethylenglicol monohexadecylether and 1420–  
17 1510 nm for those templated with D-glucose. Regarding to both bands from 1700 and 1750  
18 nm, these are shifted towards higher values, 1720 nm and 1764 nm, in PEG templated  
19 matrices and almost disappear in D-glucose templated matrices.  
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28 These aspects confirm that the carbonyl and hydroxyl groups from flavonoidic structure  
29 present in orange peel extract are involved in weak interactions (e.g. hydrogen bonding) with OH  
30 groups from surface of silica polymeric network, indicating the appearance of coupling  
31 phenomena and a conformational structural rearrangement favourable for transmission and  
32 amplification of fluorescence properties.  
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37 The effective conversion of templated silicon sol in hybrid silica materials containing  
38 orange peel extract entrapped inside the polymeric network and other information regarding to  
39 the weak interactions by hydrogen bonds type between silica-silsesquioxane network and organic  
40 molecules (flavonoidic/polyhydroxylic compounds), have been also confirmed by FT-IR  
41 spectroscopy (Fig. 3). A first observation that suggests the change of silica network as a result of  
42 extract immobilization into polymeric network pores is provided by the modification of band  
43 from  $1080\text{ cm}^{-1}$  assigned to  $\nu_{\text{Si-O-Si asym}}$  (from silica matrix spectrum) in a broad band which  
44 contains the vibration of C – OH bond of template molecule ( $\nu_{\text{C-OH template}} = 1179\text{ cm}^{-1}$  for PEG  
45 and  $1187\text{ cm}^{-1}$  for D-glucose) and  $\nu_{\text{C-OH extract}}$  at  $1200\text{ cm}^{-1}$  (in immobilized samples).  
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53 The modification of silica network after immobilization step is also evidenced by the shifting  
54 of absorption bands of O – Si – O group from  $580\text{ cm}^{-1}$  and  $446\text{ cm}^{-1}$  (for immobilized extract with  
55 PEG template),  $565\text{ cm}^{-1}$  and  $448\text{ cm}^{-1}$  respectively (for immobilized extract with D-glucose  
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3 template), as comparing with its positions in templated silica matrices (574 and 450  $\text{cm}^{-1}$  for PEG  
4 templated silica matrix; 560 and 458  $\text{cm}^{-1}$  respectively, for D-glucose templated silica matrix).

7 The implication of Si – OH bond in forming some weak interactions (hydrogen bonds)  
8 with other hydroxyl and carbonyl groups from flavones structure is evidenced by the broad band  
9 from 3450  $\text{cm}^{-1}$  and by the shifting of Si – OH band from 940  $\text{cm}^{-1}$  (in templated matrices)  
10 towards higher values in immobilized samples (948  $\text{cm}^{-1}$ ).  
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14 The fluorescence activity of orange peel extract samples immobilized in different  
15 polymeric matrices was comparatively determined with that of native orange peel extract, by  
16 measurements of fluorescence emission intensity. All the samples were excited at a wavelength  
17 specific for flavonoidic compounds ( $\lambda = 260$  nm), obtaining two characteristic emissions for  
18 native orange peel extract and immobilized extract samples, at 306 and ~450 nm (Fig. 4 and  
19 Table 1). By comparing the native orange peel extract fluorescence spectrum with those of  
20 immobilized extract spectra in inorganic silica and hybrid silica-silsesquioxane networks, a clear  
21 evidence of immobilization process can be observed (Fig. 4, table 1).  
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28 As a result of orange peel extract entrapment, in all the immobilized samples the  
29 fluorescence intensity was more than 10 times amplified due to the physical adsorption of orange  
30 peel extract (hydrogen bonds), excellent synergistic optical properties of  $\text{SiO}_2$  and silsesquioxane  
31 compound and due to favorable conformational arrangement.  
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35 An average diameter size of about hundreds nanometers for polymeric silica aggregates  
36 containing immobilized extract have been evidenced by DLS measurements. From the fig. 5 is  
37 observed that for both kinds of materials synthesized either by using silica or silica –  
38 silsesquioxane matrices, only a single peak area has been observed, with both kinds of template  
39 (PEG and D-glucose). The particle size distribution and estimation of average diameters of  
40 hybrid OPE-silica materials (suspended in ethanol) were: 587 nm and 979 nm – in immobilized  
41 samples templated with D-glucose, respectively 788 nm and 392 nm – for PEG templated  
42 immobilized samples), with a polydispersity ranging between 0.110 and 0.440.  
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49 The immobilization of orange peel extract in both selected polymeric matrices have been  
50 also demonstrated by transmission electronic microscopy, the obtained results being in good  
51 agreement with dynamic light scattering measurements. In Fig. 6 are comparatively presented the  
52 microscopy images of orange peel extract immobilized with D-glucose as template in silica  
53 polymeric matrix (Fig. 6A) and hybrid silica-silsesquioxane network (Fig. 6B). In both cases, the  
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3 size of polymeric aggregates is of about hundred nanometers, but smaller units could be also  
4 supposed, since such morphological formations induced by templating action of D-glucose could  
5 determine a size order of about tens nanometers. As expected, the polymeric silica matrix does not  
6 confer a polyhedral uniformity (Fig. 6A) as can be observed in hybrid silica-silsesquioxane  
7 network, where the polyhedral structure of silsesquioxane units is clearly outlined (Fig. 6B). The  
8 dispersion and immobilization of orange peel extract at molecular level are confirmed by  
9 advanced transparency degree of silsesquioxane units.  
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#### 18 4. CONCLUSION

19 In the present research an orange peel extract was successfully entrapped inside a silica-  
20 silsesquioxane polymeric network, using an immobilization method in mild conditions (room  
21 temperature, pH~6), which allowed the extension of immobilization process to a large variety of  
22 natural extracts (sensitive at temperature and pH) in appropriate hybrid host matrices.  
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26 The immobilization of orange peel extract in polymeric materials – as integral component  
27 of silsesquioxane network – leads to a significant improvement of the functional properties of the  
28 final material, the fluorescence signals obtained in these materials being by more than 10 times  
29 and even 20 times higher as comparing with native orange peel extract.  
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33 As a result of using some biocompatible compounds and performance of silica and hybrid  
34 silica-silsesquioxane networks in amplifying the fluorescence properties of the final materials, this  
35 immobilization process may lead to novel hybrid materials that can be used as potential candidates  
36 for application in biomedical field, e.g. as markers for imaging, diagnostic and therapy.  
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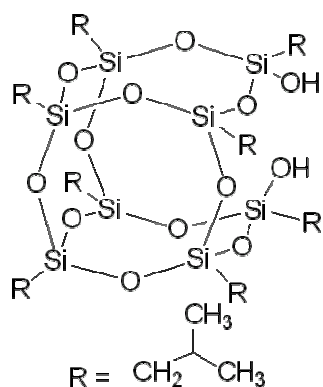
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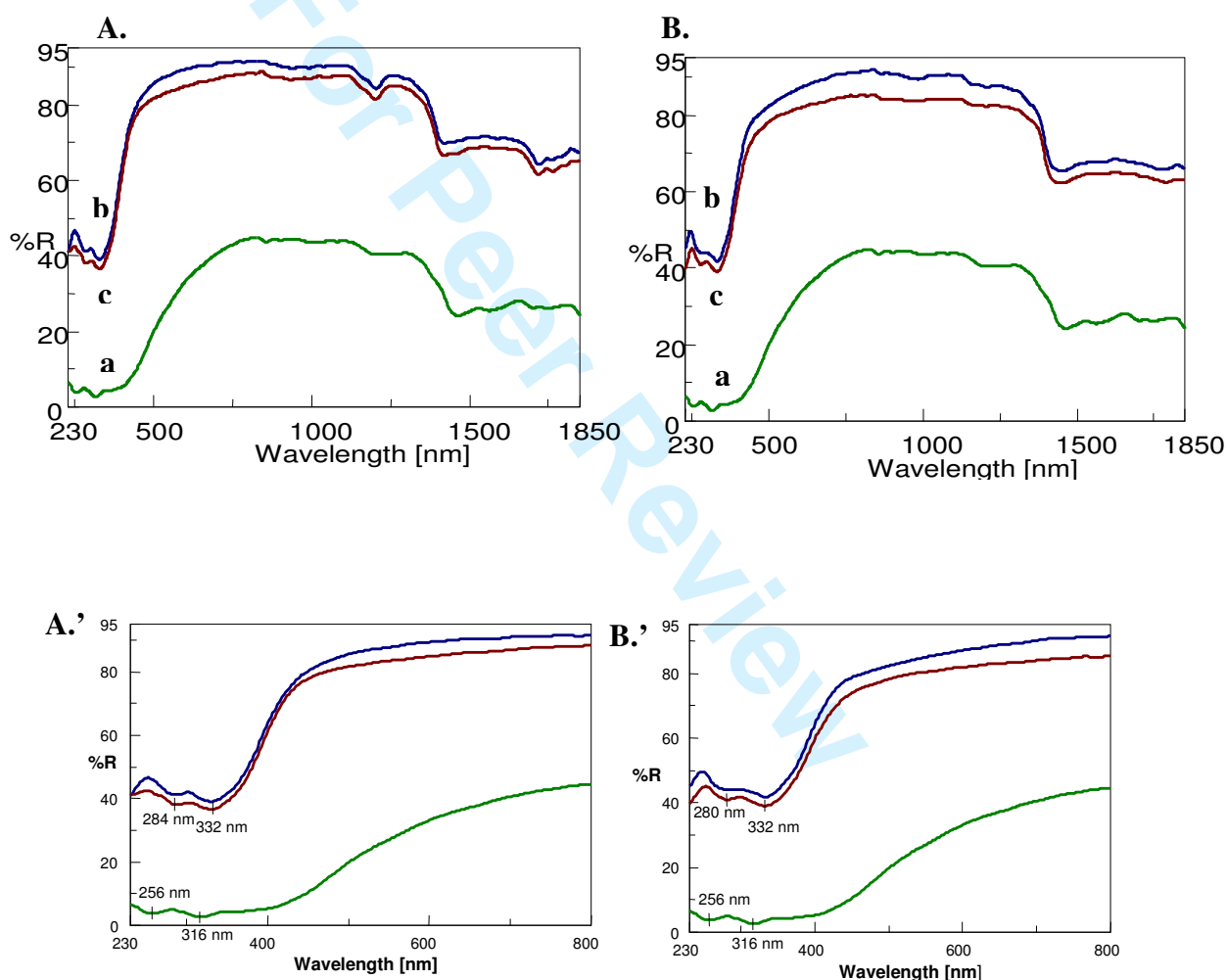
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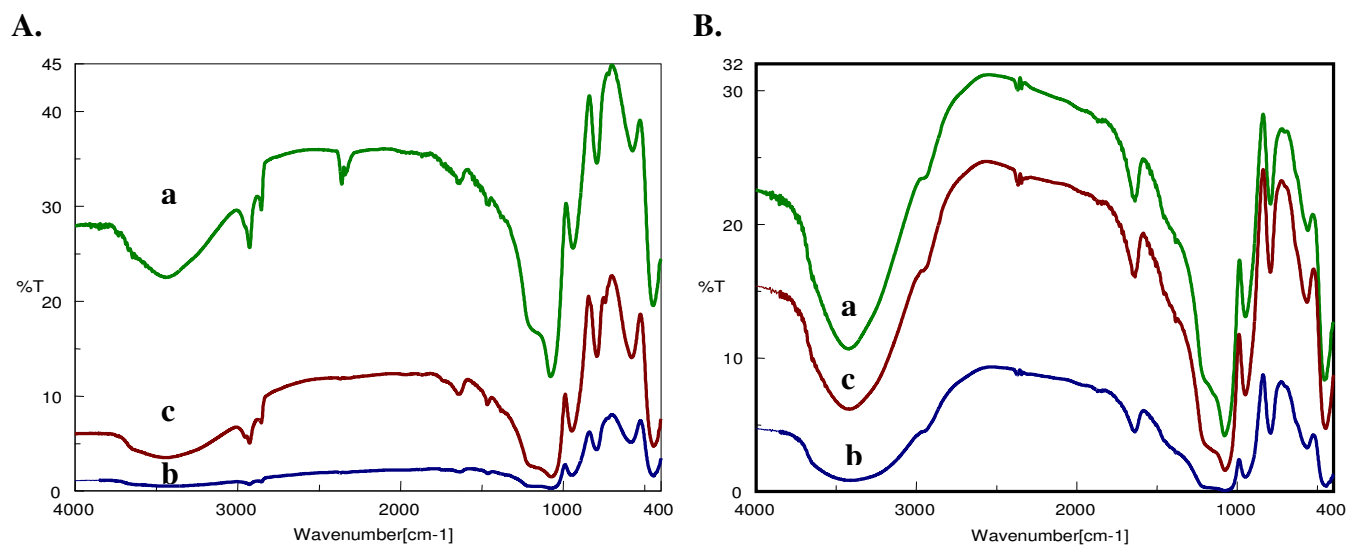
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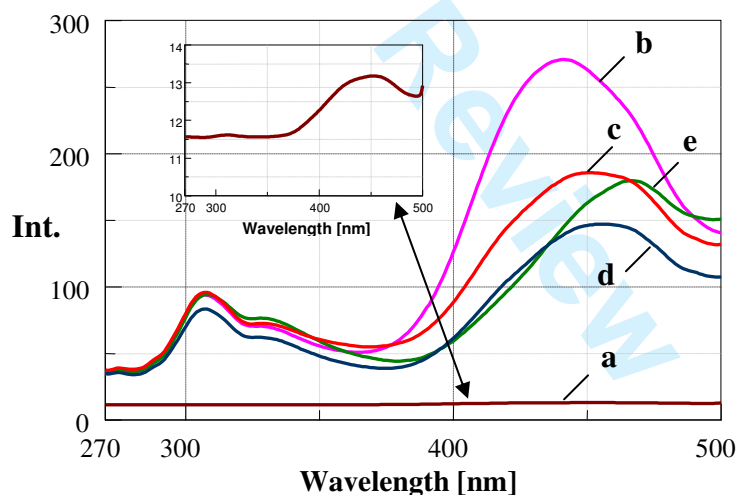
**Fig. 1.** Octaisobutyltetracyclo[7.3.3.1<sup>5,11</sup>]octasiloxane-endo-3,7-diol



**Fig. 2.** UV-VIS-NIR electronic spectra of the samples obtained with  
 A. tetraethylenglicol monohexadecylether template, B. D-Glucose template:  
 (a) native orange peel extract-OPE, (b) OPE immobilized in inorganic silica matrix,  
 (c) OPE immobilized in hybrid silica-silsesquioxane matrix  
 A' and B' contain detailed UV region of A and B figures

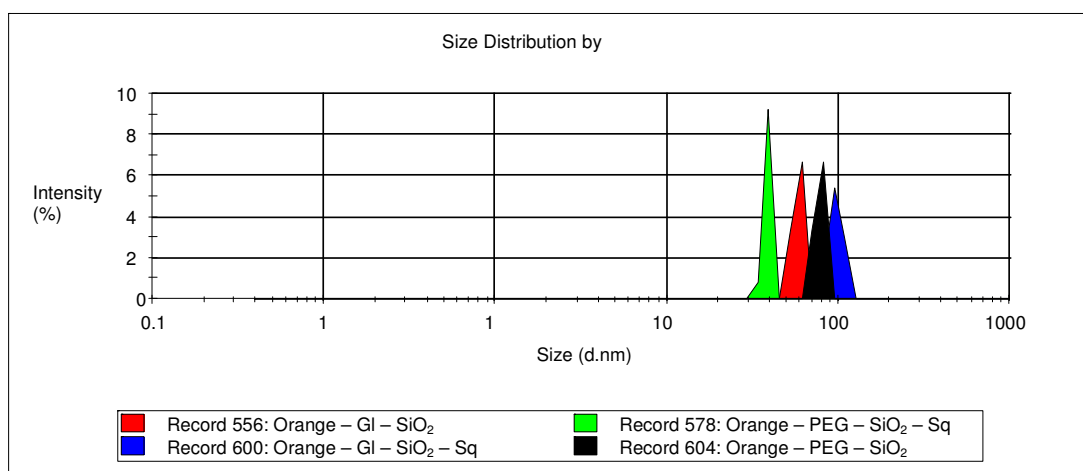


**Fig. 3.** FT-IR spectra of samples obtained with A. tetraethylglycolic monohexadecylether template and B. D-Glucose template: (a) silica matrix, (b) OPE immobilized in inorganic silica matrix, (c) OPE immobilized in hybrid silica-silsesquioxan network



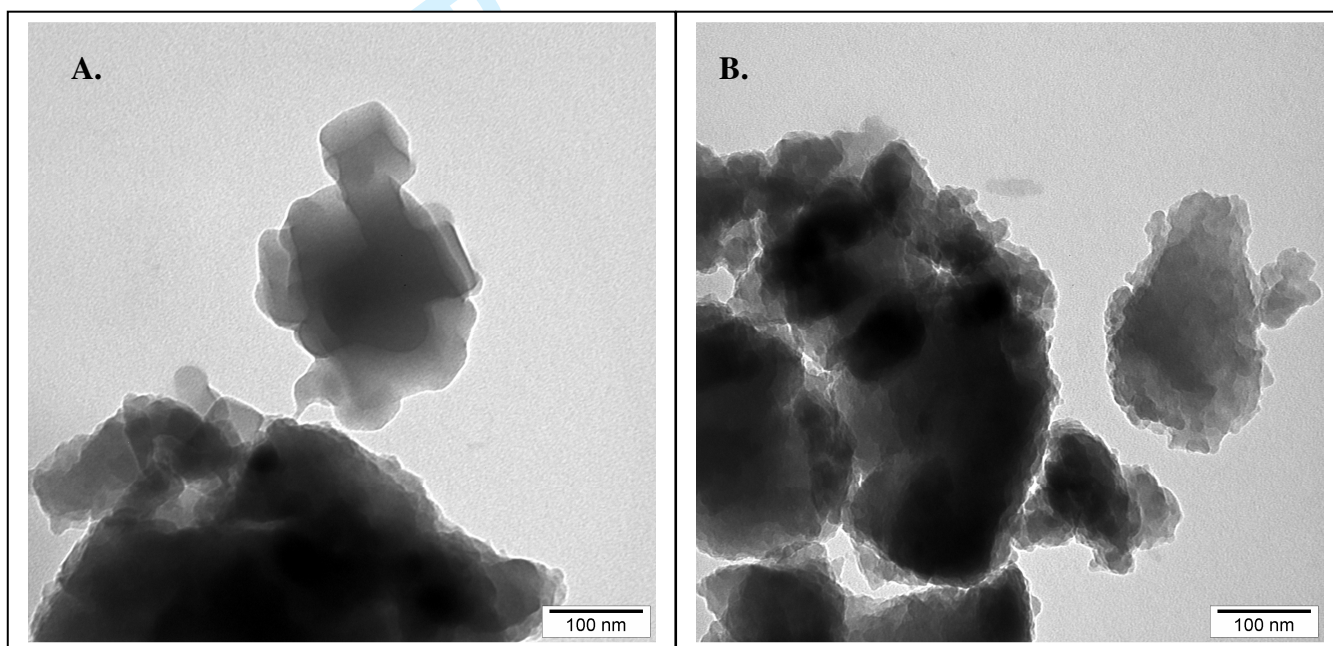
**Fig. 4.** The fluorescence properties of orange peel extract immobilized in different matrices: (a) native OPE, (b) OPE immobilized in inorganic silica matrix and (c) OPE immobilized in hybrid silica network, templated with PEG, (d) OPE immobilized in inorganic silica matrix and (e) OPE immobilized in hybrid silica network, templated with D-glucose





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**Fig. 5.** DLS measurements of orange peel extract immobilized in polymeric silica and silica – silsesquioxane matrices



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**Fig. 6.** TEM imagines of orange peel extract templated with D-Glucose and immobilized in: (A) polymeric silica matrix, (B) hybride silica-silsesquioxane network

**Table 1.** Fluorescence intensity of orange peel extract immobilized in different matrices

No	Samples	$\lambda$ [nm]	Int.	$\lambda$ [nm]	Int.
1	OPE	306	11.6	452	13.2
2	OPE-PEG-SiO <sub>2</sub>	306	93.6	442	270.5
3	OPE-PEG-SiO <sub>2</sub> -Sq	306	95	450	185
4	OPE-Glucose-SiO <sub>2</sub>	306	83.2	457	147.3
5	OPE-Glucose-SiO <sub>2</sub> -Sq	306	94.4	465	179.6

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