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# Silica Polymeric Networks Templated with D-Fructose - as Host Matrices for Natural Extracts Immobilization

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# Silica Polymeric Networks Templated with D-Fructose – as Host Matrices for Natural Extracts Immobilization

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*In the present paper a non-surfactant templating route has been employed to prepare new fluorescence nanostructured materials, by combining some natural organic molecules present in vegetal extracts with three-dimensional silica and hybrid silica-silsesquioxane networks. The results obtained clearly indicated that organic chromophores like flavonoid compounds from two extracts with bio-active principles (orange peel extract and ornamental bush extract) can be efficiently immobilised in the host silica and hybrid matrices, using D-fructose as template. The confirmation of immobilization process was demonstrated by extensive characterization of final materials, achieved based on spectroscopy technique, fluorescence intensity measurements and transmission electron microscopy.*

**Keywords** D-fructose; extract immobilization; fluorescence activity; hybrid matrices

## 1. Introduction

The incorporation of different natural extract that contain flavonoidic compounds with bio-active properties into silica polymeric matrices is a highly challenging task in the field of nanomaterials. The study of these materials represent an important step in their utilization for various bio-medical applications, since flavonoids compounds are a group of polyphenolic compounds with recognized biological activity which are present in most plants (concentrated in seeds, fruit skin or peel) [1]. These compounds are usually associated with antioxidant, anti-inflammatory, anti-tumour activities and with potential chemopreventive properties [2,3]. These aspects are also sustained by silica-based matrices that are widely used in the field of biomedicine, due to

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their chemical inertness, biocompatibility and optical transparency (being excellent photonic media) [4]. Moreover, the organic molecules entrapped in silica matrices typically exhibit improved resistance to thermal and chemical denaturation, enhanced optical properties, as well as increased storage and operational stability [5–7].

The goal of this research is to create new materials with specific optical properties by combining different three-dimensional silica and hybrid silica-silsesquioxane frameworks with two natural extracts: orange peel extract (OPE) and ornamental bush extract (OBE). They represent a reach natural source of flavonoids and their mutual arrangement at nanosize scale can be controlled by using a high biocompatible template from the glucidic class. The organo-modified silica materials have been synthesized through non-surfactant templated sol-gel route of tetraethylortosilicate and an organo-silsesquioxane compound (octaisobutyltetracyclo-[7.3.3.1$^{5,11}$]-octasiloxane-*endo*-3,7-diol), by using with D-fructose as template. This silsesquioxane precursor was chosen having in view its obviously advantages. Firstly, being an intermediate between silica and silicon $(RSiO_{1.5})_n$, this leads to a thermal and chemical robust organic-inorganic network. Secondly, it contains some unreactive organic groups (−R) for solubilization and compatibilization and other two reactive groups (−OH) for polymerization or forming H bonds. Thirdly, most important, this compound presents a cage structure (with diameter of 1–3 nm), being the smallest silica particle, usually named as ''molecular silica'' [8,9]. Therefore, it is interesting to evaluate the suitability of the new silica-silsesquioxane hybrid networks – as host matrices used for natural extract immobilization and to investigate how these matrices may preserve and even enhance the specific properties of natural extracts.

## 2. Experimental

**Materials.** Tetraethyl orthosilicate (TEOS, Aldrich, 98%); octaisobutyltetracyclo [7.3.3.1$^{5,11}$] octasiloxane-*endo*-3,7-diol (Sq, Aldrich, 97%); D-fructose (Merck); ethanol (Riedel-de Haën, 99.8%); double distilled water and nitric acid (65%, Merk). The vegetal extracts with flavonoid compounds were sampled by the authors from flowers of an ornamental bush (*Sambucus ebulus* plant, OBE) and from peel solids of orange fruits (OPE). The flavonoidic mixtures, as yellow and violet oil products, were successively extracted with warm ethanol (at 40°C), concentrated under vacuum and purified by column chromatography.

**Synthesis procedure.** For the natural extract immobilisation, a typical protocol was followed to prepare in a first stage a pre-hydrolysed templated silica sol [10,11], synthesized in acidic catalysis (pH ~ 3, t°C = 60°C, 2 h), using a molar ratio TEOS:$H_2O$:Et-OH = 1:2:4; after cooling an aqueous solution of D-fructose (2 M) was added to the sol. In the second stage, the immobilization of natural extract into inorganic silica and hybrid networks was achieved, by adding 1 mL aqueous extract in 12 g templated silica sol; in order to realize the immobilization inside a hybrid network, the octaisobutyl tetracyclo-[7.3.3.1$^{5,11}$]octasiloxane-*endo*-3,7-diol (0.005 M Sq) was added together with natural extract in prepared D-fructose silica sol. All four mixtures – which contain the extracts (OPE and OBE) and two host matrices – were sealed with parafilm (with holes) and kept under stirring for 12 h. Upon gelation and drying period (35°C, 2 days), the template silica composites are obtained as glass hybrid nanostructured materials.

**Characterization.** UV-VIS-NIR spectroscopy was used for structural analysis; the electronic spectra were recorded between 200 and 1850 nm using a Jasco

double – beam V570 Spectrophotometer. The structures of the immobilized flavonoids compounds from natural extracts were studied by FT-IR spectroscopy (4000–400 $cm^{-1}$ range, Jasco 620 FT-IR). Fluorescence measurements were carried out with a spectrofluorimeter (FP-650, Jasco). The samples were illuminated with a 260 nm excitation light and the fluorescence emission was collected at 305 nm and 420–470 nm, respectively. Fluorescence assays were performed on solid samples of native extract and immobilized extracts in the inorganic silica and hybrid silica-silsesquioxane networks. The hydrodynamic diameters of immobilized extract 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 were investigated by transmission electron microscopy using a Philips 208 S device.



## 3. Results and Discussion

One of the most unique advantages of non-surfactant approach with sugar compounds to nanostructured materials is their high biocompatibility. Instead of using surfactant as template molecules, non-surfactant small molecules, like D-fructose, are chosen to function as template. This quite minor change in the sol-gel process results in a big difference in entrapment of active molecules in the following ways: unlike surfactant molecules, especially some ionic surfactant molecules, which are toxic and expensive, the small non-surfactant molecules used as templates are biocompatible, low cost and harmless to most biological media. Fructose can be used as template firstly due to its structure that contains highly polar functional groups and thus it can work as directing agent, and secondly, due to its collectivity: the aggregates or glucidic assemblies participate to strong polar interactions and H bonds with OH groups of inorganic species (intermediate silicate species) and thus can favor or even catalyze the sol-gel reaction [12]. One of the possible explanations is based on the fact that the strongly polar interactions and the hydrogen bonds between glucidic aggregates and inorganic silica species play an important role to direct the formation of the interconnected channels.

These aspects enabled us to use a direct immobilization method of some natural extracts, like orange peel and ornamental bush extracts, inside two kinds of host matrices (inorganic and hybrid) of controlled pore diameters. The polymeric host matrices were obtained by preparing organic modified hybrid materials, starting from a pre-hydrolyzed TEOS sol to which an organo-silsesquioxane compound was added. The immobilization was performed by direct insertion of natural extract containing actives principles to non-surfactant – templating sol-gel reaction prior the gelation with pH adjusted to near neutral and partial removal of ethanol.

A first technique used for evaluation of natural extract immobilization in the two selected host matrices was UV-VIS-NIR spectroscopy. The main domains followed in order to obtain some information about the presence of natural extract inside the matrices were:

- The absorption bands from UV domain, which appear in native extract at 256 nm and 316 nm (for OPE) and 304 nm and 342 (for OBE) – assigned to carbonyl and carboxyl groups from flavonoid structure; these bands were significantly shifted towards higher/lower wavelengths in immobilized samples: 286 nm/332 nm (for OPE) and 284/328 nm (for OBE);

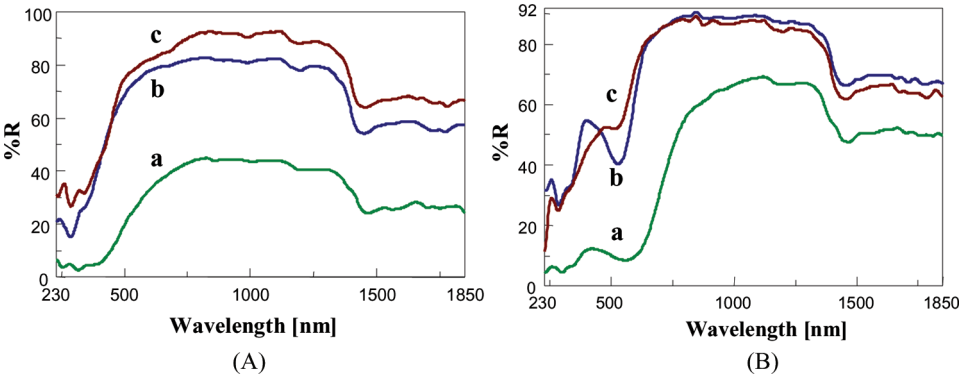


**Figure 1.** UV-VIS-NIR electronic spectra of OPE (A) and OBE (B) samples: (a) non-immobillized natural extract; (b) imobillized in inorganic silica matrix; (c) immobilized in hybrid silica-silsesquioxan matrix using D-fructose as template.

- In NIR domain, the associated and free OH groups from native extracts were observed at 1464–1562 nm and 1704–1758 nm. These bands were also shifted in all the four immobilized samples: 1452 nm and 1720–1778 nm (for samples immobilized in $SiO_2$ matrix) and ~1455 nm and 1722–1780 nm (for samples immobilized in $SiO_2$-Sq network).

All these observations represent a primary confirmation of involvement of carbonyl/hydroxyl groups from flavonoidic structure in weak interactions with free OH groups from polymeric silica network. Another evidence comes from the ornamental bush extract immobilized samples that exibit a broad band at 525 nm (558 in OBE), which can be assessed to an extensive conjugation of polyphenolic chromophoric groups.

The interaction between flavonoidic compounds from extracts and silica polymers was confirmed by FT-IR spectra. The broad peak which appears in silica matrix at 1082 $cm^{-1}$ is attributed to the asymmetric stretching motion of oxygen atoms of two adjacent Si–O–Si units. This broad band also contains the vibration band of C−OH bond (a shoulder at 1200 $cm^{-1}$). In the case of immobilized samples (Figs. 2b, c), these peaks were broadened and shifted to higher wavenumbers for C−OH bond

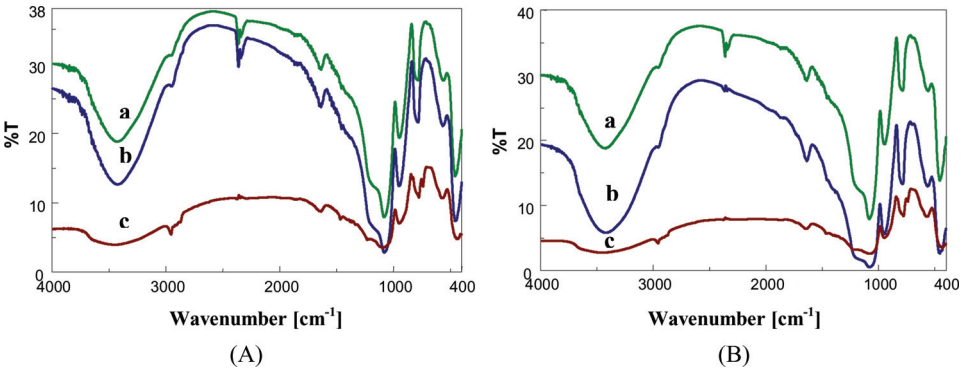


**Figure 2.** FT-IR spectra of OPE (A) and OBE (B) samples: (a) D-fructose silica matrix, without extract; (b) natural extract immobilized in inorganic silica matrix; (c) extract immobilized in hybrid silica-silsesquioxane network.

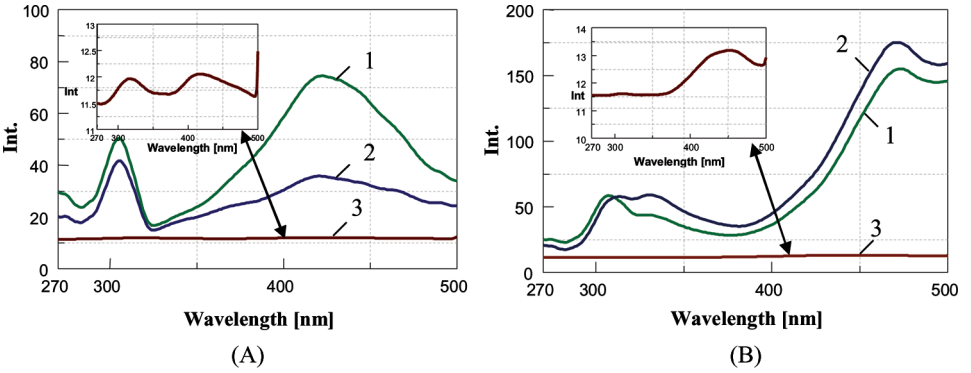


**Figure 3.** The fluorescence properties of immobilized OPE (A) and immobilized OBE (B) in: $SiO_2$ (1) and $SiO_2$-Sq (2) matrices, compared with natural extract (3).

(for OPE: 1206/1221 $cm^{-1}$ for $SiO_2$/$SiO_2$-Sq matrices). The peak from 780 $cm^{-1}$ is associated with the bending vibrational mode of symetrical Si–O–Si units.

The shift of the absorption of O–Si–O units to higher/lower wavenumbers was also observed: 566/458 $cm^{-1}$ and 574/433 $cm^{-1}$(for OPE) and 566/455 $cm^{-1}$ and 571/442 $cm^{-1}$ (for OBE), as comparing with silica matrix (561 and 458 $cm^{-1}$). These results accompanied by the broad absorption band from 3400 $cm^{-1}$and by a sligt shift of Si–OH stretching vibrational mode (from 948 $cm^{-1}$ – in silica matrix towards 950 $cm^{-1}$ – in immobilized samples) is due to O–H associated groups involved in weak interactions. It can suggest a hydrogen bond interactions as illustrated in Figure 2 between hydroxyl/carbonyl groups from flavonoid/template and silanol groups from the polymer matrices.

The fluorescence spectra of the final materials, in which the natural extracts were immobilized, are presented in Figure 3, comparing with that of native extract. As can been seen in this figure, all immobilized samples exhibited the characteristic emission bands at $\lambda = 305$ nm for OPE/307 nm for OBE of the carbonyl groups from flavonoidic structure and a broad emission band located at 450 nm for OPE/420 nm

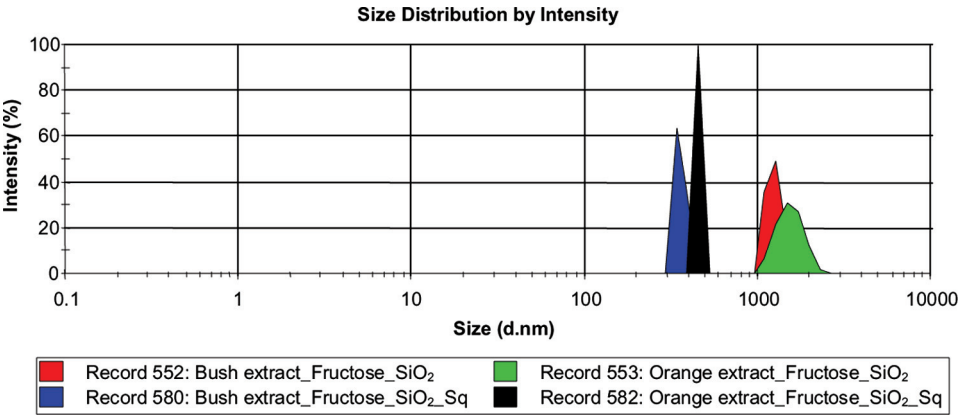


**Figure 4.** DLS measurements of natural extracts immobilized in polymeric $SiO_2$ and $SiO_2$-Sq matrices.

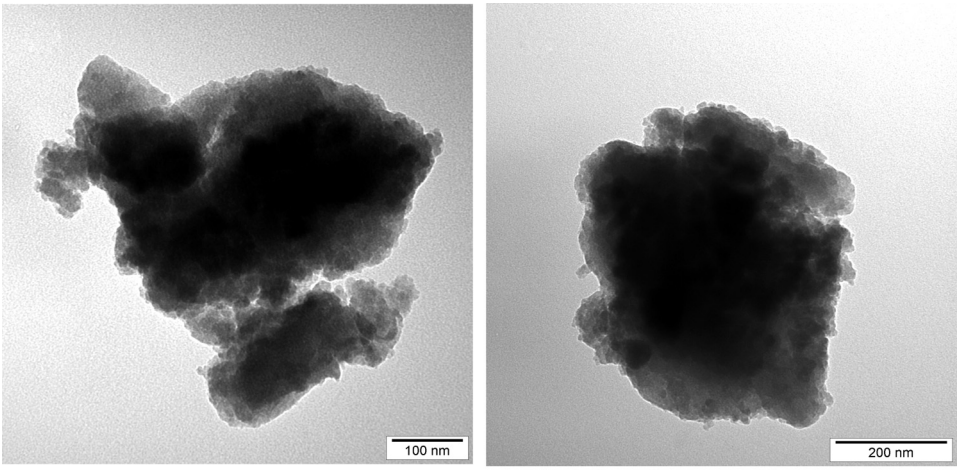


**Figure 5.** TEM imagines of natural extracts (A = OPE and B = OBE) immobilized in hybrid silica-silsesquioxane network, templated with D-fructose.



for OBE, which may be associated to an extensive conjugation of OH polyphenolic and/or glucidic groups involved in hydrogen bonds. Compared to the native extracts, both emission bands are considerably broadened and enhanced, more evidently for the second band, as a result of immobilization of natural extract in polymeric silica networks by physical adsorption. Therefore, for the emission bands from 420/450 nm, the fluorescence intensity was enhanced with cca six times for OPE and ten times for OBE, as comparing with non-imobilized extracts (Fig. 3).

These optic-active organic molecules immobilized within the channel structure of $SiO_2$ and hybrid $SiO_2$-Sq present a uniform distribution and dispersion degree in host matrix, as it was shown by dynamic light scattering measurements and electron microscopy (Figs. 4 and 5). The average hydrodynamic sizes of samples immobilized in hybrid network (322 nm for OPE and 362 nm for OBE) were less than those of samples immobilized in silica matrix (1.56 μm for – OPE and 1.25 μm – for OBE), fact that reveals the efficiency of silsesquioxane presence.

The size of hybrid materials units obtained using silica – silsesquioxane network and evidenced by TEM analysis (Fig. 5) is in good agreement with the observations from DLS measurements.

## 4. Conclusion

In the obtained polymer materials, the hydrogen bonds interactions between residual silanol groups and carbonyl and hydroxyl groups of flavonoid compounds from natural extract were confirmed by UV-VIS and FT-IR spectroscopy. We demonstrated that such hydrogen bonding interactions were strong enough to permanently integrate the natural extract as an integral component of inorganic silica and hybrid silica modified with silsesquioxane network.

Two natural extracts were successfully immobilized into silica and organically-modified silica materials using the acid-catalyzed hydrolysis and co-condensation

of tetraethylorthosilicate and silsesquioxane via the non-surfactant templated sol-gel process. Unlike many other encapsulation methods, this pathway is simple to perform, easily modified, and produces silica polymeric nanomaterials that contain flavonoid compounds in which the active principles remain active. The immobilization process suggested for entrapping of some natural extracts results in obtaining of new materials containing natural extract with enhanced fluorescence properties. The fluorescence intensity was amplified due to the physical adsorption of natural extract, excellent synergistic optical properties of silica and silsesquioxane compounds and due to a favorable conformational arrangement of natural extract inside the matrix. Based on the enhancement of fluorescence intensities, the new hybrid materials obtained may be used in construction of some functional materials with optical and biomedical applications.



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## References

[1] Malesev, D. & Kunti, V. (2007). *Serb J. Chem. Soc.*, *72*(10), 921.
[2] Fan, K., Kurihara, N., Abe, S., Ho, C. T., Ghai, G., & Yang, K. (2007). *J. Med. Food*, *10*(1), 11.
[3] Abe, S., Fan, K., Ho, C. T., Ghai, G., & Yang, K. (2007). *J. Med. Food*, *10*(1), 18.
[4] McCusker, C., Carroll, J. B., & Rotello, V. M. (2005). *Chem. Comm.*, *996*.
[5] Livage, J., Coradin, T., & Roux, C. (2001). *J. Phys. Condens. Matter.*, *13*, R673.
[6] Lacatusu, I., Badea, N., Nita, R., Murariu, A., Miculescu, F., Iosub, I., & Meghea, A. (2010). *Optical Materials*, *32*, 711.
[7] Lacatusu, I., Badea, N., & Meghea, A. (2009). *Key Eng. Mat.*, *415*, 57.
[8] Watanabe, A. & Miyashita, T. (2006). *Chemistry Letters*, *35*(10), 1130.
[9] Kim, M. S., Seok, S. I., Ahn, B. Y., Koo, S. M., & Paik, S. U. (2003). *J. Sol-Gel Sci. and Techn.*, *27*, 355.
[10] Lacatusu, I., Badea, N., Nita, R., Giurginca, M., Bojin, D., Iosub, I., & Meghea, A. (2010). *J. Phys. Org. Chem.*, *22*, 1015.
[11] Lacatusu, I., Badea, N., Bojin, D., Iosub, S., & Meghea, A. (2009). *J. Sol-Gel Sci. and Tech.*, *51*(1), 84.
[12] Wei, Y. & Qiu, K. Y. (2004). Nanoporous Materials – Science and Engineering. In: *A novel nonsurfactant route to nanoporous materials and its biological applications*, Lu, G. Q. & Zhao, X. S. (Eds.), Imperial College Press Publishers: London, 873.