

# Synthesis and characterization of a silsesquioxane nanocomposite with photoluminescence properties

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*In situ* organically-modified silsesquioxane nanoparticles with vinyl units were obtained combining the sol-gel technique and the radical polymerization of vinyltrimethoxysilane (VTMS) in the presence of a small amount of a cationic surfactant, i.e., cetyl trimethylammonium bromide (CTAB). The surfactant was added in order to improve the optical properties based on controlled nanophase separations. The hydrolysis and polycondensation reactions were followed by Fourier Transform infrared spectrometry (FTIR), Scanning electron microscopy (SEM) and fluorescence measurements.

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## 1. Introduction

During last years, hybrid organic-inorganic nanocomposites have been regarded as a new generation of high performance materials that can potentially be designed for a wide range of applications in different fields. These materials combine the advantages of their constituents like high transparency (glass-like), low processing temperatures (polymer-like), good thermal stability (silicone-like) and easy accessibility due to a unique availability of the precursors (metal alkoxides and organo-alkoxysilanes).

Trialkoxysilanes  $\text{RSi}(\text{OR}')_3$  with an organic substituent R are suitable precursors of organic-inorganic hybrid materials, serving as efficient coupling agents and, therefore, increasing compatibility between organic and silica phases. The sol-gel polymerization of trialkoxysilanes involving hydrolysis and polycondensation results in formation of (poly)silsesquioxane  $(\text{RSiO}_{3/2})_n$  products, an important class of organosilicon compounds among silicon-based materials which attain increasing interest in various fields of materials science and industrial use [1-4]. As follows, silsesquioxanes are used in various applications such as precursors for highly defined  $\text{SiO}_2$  films (used for electrical insulation, anti-reflective coatings and optical filters), in the production of specialized silicon oxo-carbide ceramics or in the formation of inorganic-organic hybrid materials [5-7].

Like many other organo-silicon compounds, silsesquioxanes show an efficient photoluminescence [8, 9]. Unlike currently common organo-silicon compounds with chain or "ladder" structure, in which the photoluminescence is associated with the  $\sigma^* - \sigma$  transition, silsesquioxanes show much higher photochemical stability and their photoluminescence does not show any photo-degradation under similar conditions. Therefore, silsesquioxanes may be regarded as alternative materials

for applications in the field of opto-electronic devices, especially for light-emitting structures with reduced dimensions [10].

In this paper, a hybrid nanocomposite with silsesquioxane and vinyl units obtained combining the sol-gel technique and the radical polymerization of vinyltrimethoxysilane, a standard sol-gel precursor, in the presence of a cationic surfactant, i.e., cetyl trimethylammonium bromide was prepared in order to evaluate the compound as a platform for opto-electronic devices. The surfactant was added in order to improve the optical properties based on controlled nanophase separations.

## 2. Experimental

### 2.1. Synthesis of hybrid nanocomposite with silsesquioxane and vinyl units (VTMS\_NaOH)

The hybrid nanocomposite was obtained combining the sol-gel technique and the radical polymerization of VTMS, in the presence of azobisisobutyronitrile (AIBN) and cetyl trimethylammonium bromide (CTAB) in basic conditions (pH = 9). As follows, the compound was prepared from a starting solution containing VTMS, a small amount of CTAB below critical micelle concentration (cmc), implying mesoscale homogeneity of the starting solution and AIBN (used as thermal initiator of the organic polymerization, 2 wt% vs. VTMS). The silica sol was prepared by mixing VTMS, ethanol, water and sodium hydroxide in a molar ratio of 1 VTMS: 10 ethanol: 3  $\text{H}_2\text{O}$ : 0.004 NaOH: 0.003 CTAB. The sample was prepared and stirred at 50° C for 3 days. After solvent evaporation, the obtained white powder was dispersed in water in an ultrasonic bath, for 30 seconds, to get a

stabilized suspension that was further dropped to a glass and left to dry.

## 2.2 Measurements

FTIR spectra were performed on a Bruker Vertex 70 instrument, in the 400–4000  $\text{cm}^{-1}$  region, 64 scans, at room temperature, using the KBr pellet technique and the Opus 5 FTIR Software. The SEM micrographs were obtained with a Quanta 200 scanning probe microscope, the specimens being fixed with adhesive past on Al conducting supports of cylindrical shape and then sputter-coated with gold. The fluorescence spectra were obtained at room temperature (without correction) with an equipment containing a double monochromator with diffraction network of the GDM-1000 type, a compensatory printer of the K-201 type and a selective amplifier. The absorbance measurements were made using a UV/vis Specord M42 spectrophotometer.

## 3. Results and discussion

Through radical polymerization and sol-gel reaction of VTMS, in the presence of AIBN and CTAB, a hybrid nanocomposite with silsesquioxane and vinyl units (VTMS\_NaOH) was obtained. The FTIR spectrum of VTMS\_NaOH hybrid nanocomposite is shown in figure 1. As follows, a characteristic strong and broad band appeared at around 3435  $\text{cm}^{-1}$  corresponding to O–H stretching vibrations of the hydroxyl groups due the strong hydrogen bond of intramolecular and intermolecular type, bounds that play an important role in such conformational arrangements [6, 11, 12]. The C–H alkyl stretching bands can be observed around 2960–3060  $\text{cm}^{-1}$ , while the absorption peaks from 1603  $\text{cm}^{-1}$  may be attributed to the unreacted vinyl groups. The spectrum shows a well defined C–H absorption of  $\text{CH}_3$  deformation at 1278  $\text{cm}^{-1}$ , while the peak at 1410  $\text{cm}^{-1}$  is characteristic of alkyl CH deformations. The presence of Si–O–Si linkages is supported by the sharp, intense absorptions at 1132  $\text{cm}^{-1}$  and 1039  $\text{cm}^{-1}$  and distinct vibrations at 443 and 543  $\text{cm}^{-1}$  (bending), while the band from 761  $\text{cm}^{-1}$  is associated with the stretching vibration mode of Si–C (unreacted Si–CH=CH<sub>2</sub> groups from vinylsilsesquioxane). The peak from 963  $\text{cm}^{-1}$  confirmed the presence of Si–OH from incompletely condensed silsesquioxane.

The formation of crystalline or amorphous silsesquioxanes with complex (T cubelike or ladderlike) structures, either polyhedral or ladder, may be inferred from FTIR spectroscopy observing the location of bands which characterize the antisymmetric Si–O–Si stretching vibrations (1200 – 1000  $\text{cm}^{-1}$ ). The appearance of a single band centered near 1120–1130  $\text{cm}^{-1}$  may be taken as a good evidence of a polyhedral structure [13], while the presence of two bands centered near 1040 and 1120–1130  $\text{cm}^{-1}$  is characteristic of a cis-syndiotactic ladder configuration [13, 14]. At the same time, other different structures are frequently proposed, i.e., randomly connected three-dimensional networks of trifunctional

monomers, ladder structures, and a combination of linear, ladder, and cagelike fragments. The appearance of two bands centered at 1132  $\text{cm}^{-1}$  (stretching) and 1039  $\text{cm}^{-1}$  (flexing) marks out the cis-syndiotactic ladder configuration formed through Si–O–Si bonds.

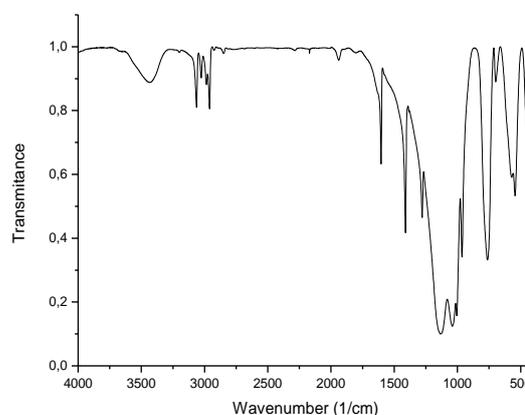


Fig. 1. FTIR spectrum of VTMS\_NaOH hybrid nanocomposite.

SEM characterization was conducted in order to evaluate the morphology of the hybrid nanocomposite (Fig. 2). SEM micrographs of VTMS\_NaOH compound at different resolutions (10  $\mu\text{m}$ , 2  $\mu\text{m}$ ) are presented in Fig. 2. As can be seen, the surfactant directed the silsesquioxanes into 3-D spherical nanoparticles ranging from 80–350 nm. would not be expected at high surfactant concentrations.

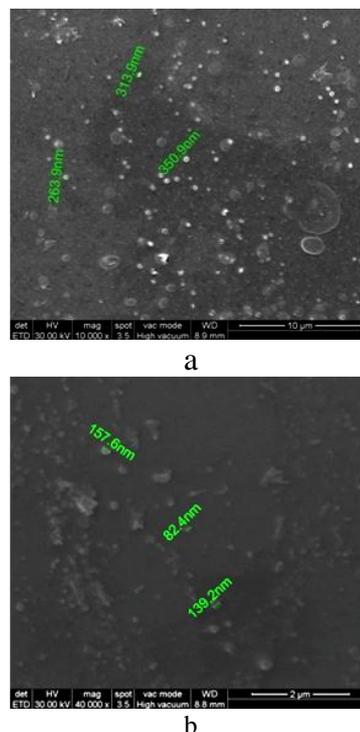


Fig. 2. SEM photographs of VTMS\_NaOH hybrid nanocomposite at different resolutions: a) 10  $\mu\text{m}$ , b) 2  $\mu\text{m}$ .

In the preparation procedure, cationic cetyltrimethylammonium (CTA<sup>+</sup>) surfactant and silica precursor (VTMS) act as templates to construct the silsesquioxane nanoparticles with well defined morphology. The surfactant molecules presumably provide a structure-directing effect for the growth of more complex structures rather than simply facilitating aggregation and coalescence of initially formed spherical nanoparticles (each cubic silsesquioxane unit - 0.5-0.7 nm - can be regarded as being nearly spherical in shape [15]), which

In general, emission spectra of silsesquioxane show two bands: monomer fluorescence band I and dimer or excimer band II. The I-st emission band is due to a charge transfer from the Si-O cage to the alkyl ligands, while the second emission band is most probably due to dimers or excimer formation [8]. The excited silsesquioxanes can interact with the ground state molecules and form excimers. Since silsesquioxanes are rather rigid molecules, intramolecular excimers seem to be rather unlikely. Nevertheless, the formation of intermolecular excimers may occur. Due to the charge transfer in the excited state these molecules show some negatively charged ligands which may for example interact with another molecule in the ground state. In figure 3 the fluorescence spectrum of VTMS\_NaOH compound ( $\lambda_{ex} = 328$  nm) in dimethyl formamide (DMF) can be observed. The emission spectrum of VTMS\_NaOH solution evidences both monomer (375 nm, 407 nm) and excimer fluorescence (434 nm). As follows, the monomer fluorescence band I can be attributed to a charge transfer transition from the non-bonding oxygen orbitals of silsesquioxanes to the lowest unoccupied molecular orbital (LUMO) of vinyl units, while band II is presumed to originate from an intermolecular excimer or an exciplex („excited complex”) as a result of intermolecular interaction.

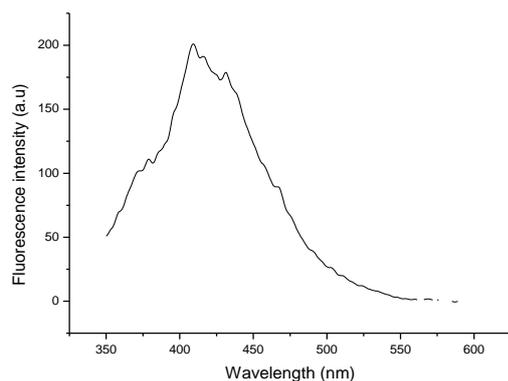


Fig. 3. Fluorescence spectrum of VTMS\_NaOH hybrid nanocomposite ( $\lambda_{ex} = 328$  nm, DMF).

### 3. Conclusions

The technique based on sol-gel polymerization and sol-gel reaction described in this paper represented a versatile synthetic approach to obtain hybrid nanocomposites with tailor-made composition of both the organic core and the

silica or organo-silica shell. Thus, spherical silsesquioxanes nanoparticles (80-350 nm) of ladder type with vinyl units were obtained. Due to photoluminescence properties, such type of compounds can represent promising candidates for designing highly luminescent light-emitting structures or can allow monitoring or metal atom extraction from solution environments. Further investigations are needed to quantify the potential of the hybrid nanocomposite for these types of applications.

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### References

- [1] M.M. Pereira, J.R. Jones, R.L. Orefice, L.L. Hench, *J. Mater. Sci.: Mater. Med.* **16**, 1045 (2005)–1050
- [2] C. Montserrat, J.S. Antonio, V.R. María, *Chem. Mater.* **18**, 5676 (2006).
- [3] E. Chiellini, A. Corti, S. D’antone, R. Solaro, *Prog. Polym. Sci.* **28**, 963 (2003).
- [4] A.P.V. Pereira, L.V. Wander, R.L. Orefice, *J. Non-Cryst. Solids* **273**, 180 (2000)–185
- [5] R.H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev.* **95**, 1409 (1995).
- [6] C.X. Zhang, F. Bavonneau, C. Bonhomme, R.M. Laine, C.L. Soles, H.A. Hristov, A.F. Yee, *J. Am. Chem. Soc.* **120**, 8380 (1998).
- [7] P.A. Agaskar, *Chem. Commun.* 1024-1026 (1992)
- [8] D. Azinovic, J. Cai, C. Eggs, H. Konig, C. Marsmann, S. Veprek, *J. Luminescence* **97**, 40 (2002).
- [9] C. Ossadnik, S. Vepřek, H.C. Marsmann, E. Rikowski, *Monatshefte für Chemie* **130**, 55 (1999).
- [10] G. Ferenczy, A. Toth, I. Bertoti, S. Suhai, *J. Phys.: Condens. Matter.* **9**, 4781 (1997).
- [11] A. Provas, M. Luft, J.C. Mu, A.H. White, J.G. Matison, B.W. Skelton, *J. Organometallic Chem.* **565**, 159 (1998).
- [12] G. Andrade, E.F. Barbosa-Stancioli, A.A. Piscitelli Mansur, W.L. Vasconcelos, H.S. Mansur, *Biomed. Mater.* **1**, 221 (2006).
- [13] J. D Miller, K.P. Hoh, H. Ishida, *Polym. Compos.* **5**, 18 (1984).
- [14] J. F. Brown, *J. Am. Chem. Soc.* **87**, 4317 (1965).
- [15] A. J. Waddon, E. B. Coughlin, *Chem. Mater.* **15**, 4555 (2003).

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