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Ionic Silsesquioxanes: A Versatile Tool to Architect Multifunctional Nanostructured Materials

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The ionic silsesquioxanes are hybrid polymers formed from the polycondensation of organoalkoxysilane precursors that contain charged groups, such as ammonium quaternary salts, where the silica network is combined with the charged organic moiety in a molecular level. These charged polymers present very peculiar characteristics such as self-organization, ionic exchange, water solubility, capacity to form strong adhered films over metal oxide surfaces and ability to stabilize metal nanoparticles. These characteristics open the possibility to synthesize or modify materials producing several multifunctional nanostructures and our research group has been devoted great attention to these systems in the last years. Here, we give an overview of the research activities of the Laboratory of Solids and Surfaces using the ionic silsesquioxanes in the development of nanostructures and nanodevices.

Keywords: silica based hybrid materials, POSS, macromolecules, nanomaterials

1. Introduction

In the material chemistry world exist inorganic, organic or hybrid macromolecules that are so amazing in their properties that allow the design and manufacture of many different systems or materials with configurations that cover from nanoparticles to bulk solids. Among these macromolecules, stand out the silsesquioxanes, which are hybrid polymers formed from the polycondensation of organoalkoxysilane precursors.[1-5] These polymers are formed by oligomeric silica networks combined with organic moieties, where these organic and inorganic components are dispersed at a molecular or nanometric level. The chosen organic moiety plays an important role, since it markedly influences the physico-chemical properties of the resulting polymer. When the organic group is an ionic one, the hybrid polymer presents very peculiar characteristics such as self-organization, ionic exchange, solubility in high dielectric constant solvents, capacity to form films over some metal and metal oxide surfaces. These characteristics opened the possibility to modify surfaces or to synthesize many multifunctional nanomaterials, which were applied in several areas such as catalysis, photocatalysis, antimicrobial systems, electrolytes for solid-state lithium ion batteries, sensors, among other applications.[6-10]

Our research group has been devoted great attention in the last fifteen years to ionic silsesquioxanes synthesized from the one step polycondensation of ionic organoalkoxysilane precursors, along with some hybrid materials derived from these systems. Besides, in our studies we developed new ionic silsesquioxanes and created new possibilities of applications in areas where they were not used yet. In this way, we are sharing here the main reports.

2. Synthesis of the Ionic Silsesquioxanes

The name silsesquioxanes came from the $R_xSiO_{1.5}$ minimum formula, where R is an alkyl group, and the oxygen/silicon ratio is 1.5 considering a complete reticulation. If R is bonded in a pendant form, the $x = 1$, however, if it is bonded in a bridged way, the $x = 0.5$.[1,4,5,11] Better explaining: "sil" corresponds to silicon, sesqui corresponds to 1.5 ratio and "oxane" is related to the oxygen (Si–O bond). The silsesquioxanes are obtained from the polycondensation of organoalkoxysilane precursors, represented in Scheme 1 for a R pendant.

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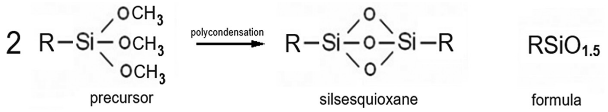
We are very honored to participate in this special issue in tribute to the memorable Professor Oswaldo Luiz Alves, who directly influenced many researchers in Brazil and abroad. His legacy will be in our minds forever, not only by his outstanding research activities, but also by his amazing classes.



Scheme 1. Representation of the silsesquioxane production.

When the organic chain presents electrically charged groups, such as ammonium quaternary salts, they are called ionic silsesquioxanes. Although there are ionic silsesquioxanes obtained from the functionalization of commercial or previously prepared POSS (polyhedral oligomeric silsesquioxanes), these systems will not be addressed here. Nevertheless, the organosilane precursors containing ionic groups were not available nearly two decades ago, and nowadays they also are not commonly commercially available. Therefore, the synthesis approach of ionic silsesquioxanes involves also the synthesis of ionic organosilane precursors.

In this way, our lab has obtained novel silsesquioxanes containing the pendant 1-azonia-4-azabicyclo[2.2.2]octane chloride group[12,13] and also the bridged 1,4-diazoniabicyclo[2.2.2]octane chloride one.[14-16] These precursors were obtained by using the nucleophilic reaction attack of basic nitrogens from diazabicyclo[2.2.2] octane to the α-carbon of halide alkyl organosilane. The preparation of both ionic silsesquioxanes is represented in Scheme 2.

The ionic silsesquioxanes were discovered by chance in the late nineties. It has been said that the hybrid silica material, which contained the pyridinium chloride group, was left overnight in water and the next day it had vanished. Actually, it was later discovered that it had dissolved and, from this point on the ionic silsesquioxane had been born.[17,18]

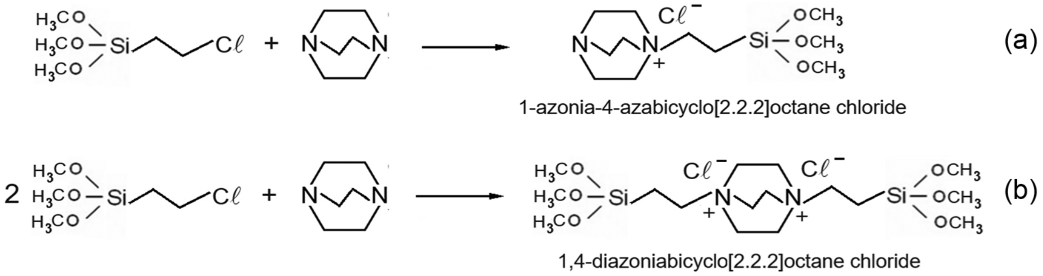
3. Properties

3.1. Self-organization property

Self-organization in chemistry is also called self-assembly and it is a spontaneous order which is caused by a process where some form of order arises from local interactions between parts of an initially disordered system. The process is spontaneous, not needing control by any external agent.[19] Self-organization has been observed in some hybrid materials or bridged silsesquioxanes and confirmed by X-ray diffraction (XRD) analysis, being that in those cases the ordered structure was caused by the rigidity of the organic chains or by interactions between them.[20,21] Some of these bridged silsesquioxanes did not exhibit well defined Bragg peaks, however, they present broad signals corresponding to the existence of a short-range order in the hybrid material.[22] This self-organization can be obtained in nano or even in micro structural levels that produces optical birefringence that can be observed by light polarized microscopy.[22,23] It is known from the literature that most of the silsesquioxanes have been shown to be layered or ladder-like long-range structures.[24,25] Cages $(SiO_{1.5})_8$ with cubic arrangement were also reported[25,26] by using also one step polycondensation. These nanostructures were named as POSS (polyhedral oligomeric silsesquioxane).

The possibility to prepare ordered structures in hybrid materials containing pendant ionic organic groups such as quaternary ammonium,[27] imidazolium or protonated amine groups were obtained nearly 20 years ago.[27,28] A layered polysiloxane containing alkylammonium groups was synthesized by sol-gel method using 3-aminopropyltrimethoxysilane (APTMS) as precursor and hydrochloric acid acting as catalyst and converting amine in ammonium groups. This reaction system provided a new synthesis method for charged layered polysiloxane materials.[29]

Based on the self-organization imposed by the electrostatic interaction of the pendant ammonium groups, our research group proposed[30] an innovative series of layered hybrid materials prepared with tetraethylorthosilicate (TEOS) and APTMS varying the TEOS/APTMS molar ratio between 1 and 3. These materials presented varied basal distances between 2.7 and 5.4 nm.[30] The structure of the materials is constituted by layers formed by six-membered ring silicates assembled in a hexagonal pattern, containing amorphous silica settled in the interlayer space, as depicted in Figure 1, along with



Scheme 2. Representation of the ionic (a) pendant and (b) bridged organosilane precursors preparing.

the XRD pattern and a transmission electron microscopy (TEM) image. This innovative singular structure brings about important properties such as interlayer distance, surface area and water solubility, which are controlled by the silica/silsesquioxane ratio.[30] Considering the surface area, the higher value obtained was 550 $m^2\ g^{-1}$ for the material with the higher silica content. The decrease in the silica content significantly reduces the surface area to values lower than 60 $m^2\ g^{-1}$. On the other hand, the water solubility decreases with the increase of the silica content, varying from 14.7 to 0.7 $g\ L^{-1}$ for TEOS/APTMS ratio 1/1 to 3/1, respectively. It is important to point out that the silica presence makes the handling of the hybrid material enlarging the possibilities of applications.

Concerning the bridged ionic silsesquioxanes, the first synthesis was reported in 2006 by our research group[14] where a bridged silsesquioxane containing an ionic 1,4-diazoniabicyclo[2.2.2]octane group was prepared. This silsesquioxane was incorporated in silica varying the amount of organics up to 5%. In that paper, it was seen that the average pore size, which was probed by small angle X-ray scattering, is compatible with the organic chain length, about 1.5 nm. Also, the surface area was dependent on the organic amount added.[14] In sequence, silica based materials with higher grade of ionic bridged silsesquioxane precursor, between 5 and 100% were prepared.[15] When the concentration of the organic precursor was increased, starting from 60%, broad diffraction peaks at 6.2° and 12.5° angles (Cu Kα) arose in the XRD pattern, as shown in Figure 2a. These peaks correspond to interplanar spaces assigned, respectively, as $d_1 = 1.43$ and $d_2 = 0.71$ nm, revealing a long-range structural order. Density functional theory calculations showed 1.38 nm as the average longitudinal oxygen bonded to silicon distance, which corresponds to the size of the organic molecular precursor bis-3-*n*-propyltrimethoxysilane (1,4-dizoniabicycle [2.2.2]octane) chloride used in the synthesis of this ionic silsesquioxane.[15] Considering these results we assumed a layered structure, as commonly reported for neutral bridged silsesquioxanes.[31-33] However, the short and long-range order structures for the ionic silsesquioxanes need to be precisely elucidated yet and they are subject of current studies.[25,34]

In these hybrid materials first order optical birefringence was observed by using polarized light optical microscopy, at different angles, as depicted in Figures 2c and 2d. This result is evidence of the anisotropic self-organization imposed by the ionic silsesquioxane presence.

3.2. Water solubility and adhesion to metal oxide surfaces

A singular characteristic of the ionic silsesquioxanes that distinguish them from the neutral ones is its solubility in solvents with high dielectric constant, such as water, methyl and ethyl alcohols. A series of hybrid silica-based materials were obtained from the polycondensation of the pendant 3-*n*-propyl-1-azonia-4-azabicyclo[2.2.2]octane chloride silsesquioxane and TEOS as precursors, varying the TEOS/silsesquioxane molar ratio from 0 up to 1.5.[12] In the absence of TEOS, the water solubility of the ionic silsesquioxane at 25 °C was 188 $g\ L^{-1}$, as the TEOS/silsesquioxane molar ratio increases to 0.33 the solubility decreases to 17.5 $g\ L^{-1}$ becoming insoluble when the molar ratio reach 1.5. This behavior was interpreted taking into account two reasons: (*i*) the size of the formed oligomers depends on the TEOS/silsesquioxane molar ratio, which decreases as the organic amount increases, increasing the solubility. The organic groups avoid random propagation of the silica network; (*ii*) the ion-dipole interactions between the ionic silsesquioxane groups present in the oligomers and the polar solvents like water.[12] These features were already reported by other authors[9,17]

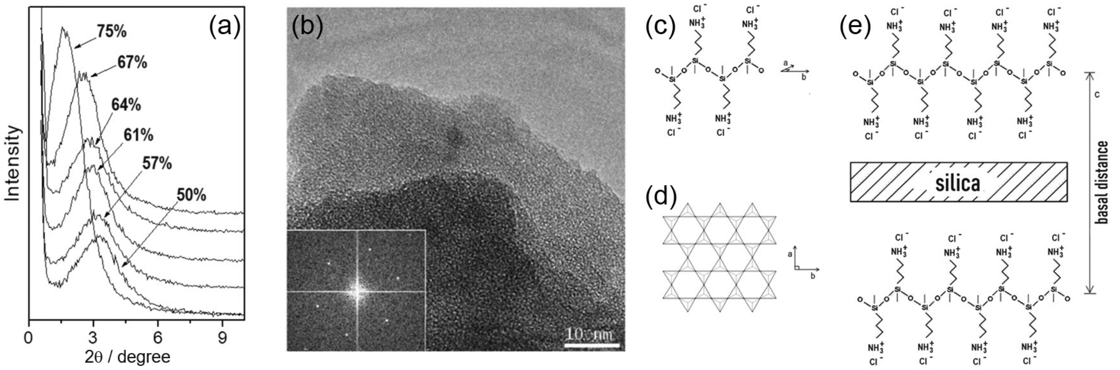


Figure 1. Proposed layered aminoalkylsilica hybrid material: (a) XRD patterns of the material series varying the grade of silica; (b) TEM image of the 75% silica grade sample, the inset Figure 1b shows the selected area of electron diffraction pattern (SAED); (c) layered ionic silsesquioxane; (d) top view of Si–O hexagonal layer of layered ionic silsesquioxane; (e) vertical cross-section showing the layered structure of the aminoalkylsilica hybrid material (Figures 3, 6 and 7 reproduced from reference 30 with copyright permission from SBQ).

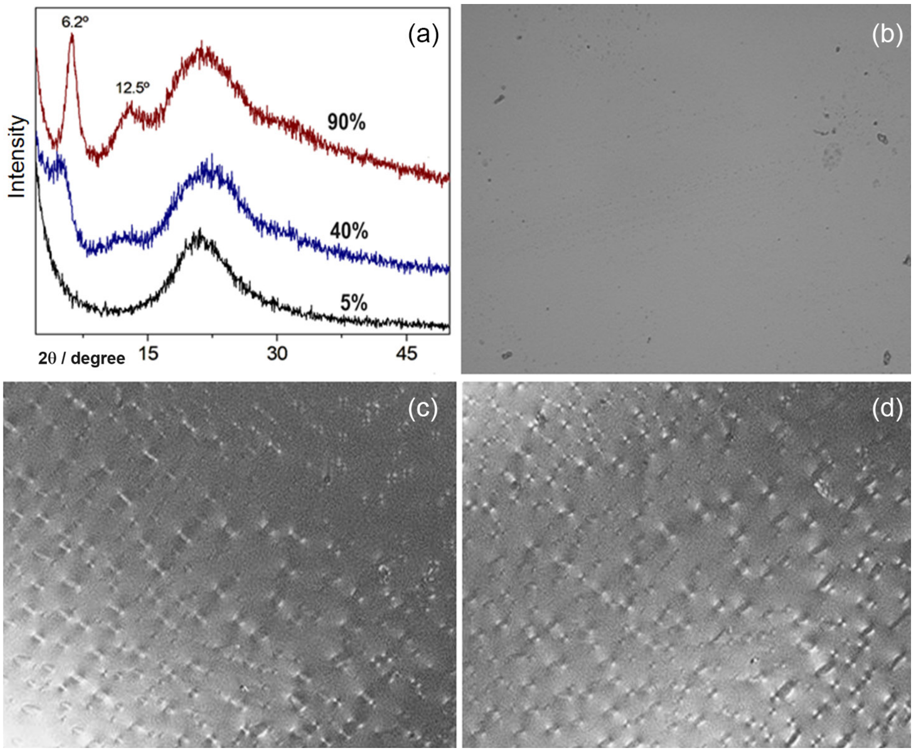


Figure 2. (a) XRD pattern of hybrid silica materials containing different grades of ionic bridged silsesquioxane. Images of hybrid material, containing 60% of bridged silsesquioxane grade, obtained in normal light (b) and in polarized light (c) 30° and (d) 60°. The widths of each image (b), (c) and (d) is 1.0 mm.

for pendant silsesquioxane containing pyridinium group. Depending on the application, the solubility can be decreased using a two steps process where an oligomeric hybrid silica/chloropropyl material is firstly prepared, followed by a functionalization with pyridine or other nitrogenated bases to produce ionic silsesquioxanes.[35] Solubility is a very important characteristic, since it allows the dispersion of silsesquioxane in solid flat surfaces, and makes easy its diffusion also into the pore of solid matrices forming very stable thin films. The stability is due to the ability of silanol groups of the silsesquioxane to react with some metal oxide surfaces resulting in covalent bond, providing high thermal stability to the organic groups (up to 300 °C).[12,13] For the aluminum oxide containing systems, the formation of a very stable bond Si–O–Al was evidenced by ^{29}Si nuclear magnetic resonance[18,36] and infrared.[37] This strong adherence inhibits the silsesquioxane leaching from the matrix when compared to the silica surface itself.[12] As an example, a silica-based thin film of high transparency containing the bridged ionic diazoniabicyclo[2.2.2]octane chloride group was prepared by an optically monitored dip coating method. The films showed homogeneity, surface uniformity, low absorption in the visible spectrum range, refraction index between 1.43 and 1.5, which allow application for anti-reflection of high index, being promising for optical applications.[38] This allowed the design of many different systems such as suspensions of oligomeric species, metal nanoparticles stabilization, deposition of films, modification of surfaces and some examples will be presented in sequence.

3.3. Ionic-exchange

Regarding the ionic silsesquioxanes present charged organic chains, usually cationic ammonium quaternary groups, they also have a counter ion (Scheme 2). In general, the counter ions are halides, since the available organosilane precursors, for the silsesquioxanes synthesis, are the alkyl halides, as previously discussed. This feature provides the anion exchange property, enlarging the possibilities of their applications, because several types of anions can be added bringing different types of properties as follows. It was reported the chloride ion-exchange by: anionic electroactive species, such as hexacyanoferrate[14] and copper tetrasulfonated phthalocyanine;[39] hydrophobic long chain carboxylate anions such as stearate, oleate or linoleate;[40] hazardous anionic species such as Cr^{IV},[41] brilliant yellow and reactive red 194 dyes[42,43] acting therefore as adsorbent for these species.

4. Stabilization of Metal Nanoparticles

Metal nanoparticles show unique chemical, physical, optical, magnetic and electrical properties that remarkably differ from the bulk metals and these properties arise from their low size. The interest in metallic nanoparticles has been growing in recent decades, because they have been used in a wide range of technological applications,[44] such as catalyst for fine chemical compound,[45,46] efficient antimicrobial dispersions, films and solid without cause resistance;[47-51] as optical, chemical and electrochemical sensors,[52-54] mainly for medicine imaging and diagnoses[55-60] as well as to improve the performance of photovoltaic devices.[61,62]

The noble metal nanoparticles synthesis can be performed by the chemical reduction of metallic ions in liquid medium, using several reducing agents like citric acid, boron hydride, hydrogen among others.[63,64] The synthesis of the noble metal nanoparticles should be made in the presence of stabilizers, because due to their high surface area there exists the thermodynamic tendency of unwanted size increasing or agglomeration. A great variety of stabilizers such as polymers, biopolymers, dendrimers, micro-emulsions, ionic liquids, surfactants or chelating agents was already reported.[63,64] Two main mechanisms of stabilization have been described, the first is called electrostatic stabilization that is based on the Coulombic repulsion produced by the charged double layer of ions interacting with their surface, and typical examples are the ionic liquids.[64] The second one is called steric stabilization and is attained by the adsorption of organic species that act as protective layers over the metallic surface. Water soluble polymers are examples of this kind of stabilization.[64] In this way, the newly formed metal nanoparticles are separated from each other, and agglomeration and growth are prevented. The choice of the synthesis conditions for the metal nanoparticles will determine their size, size distribution, the shape and consequently the optical properties.

As the ionic silsesquioxanes present an ionic part, and also a silica oligomeric network they can act as metal nanoparticles stabilizer by both mechanisms. Better explaining, the ionic part promotes the water solubility and the stabilization by electrostatic repulsion, on the other hand the silica moiety causes the adhesion to the surface and the steric mechanism. The bridged silsesquioxane containing the 1,4-diazoniabicyclo[2.2.2]octane chloride group, without any other component, was successfully applied as a gold nanoparticle stabilizer.[65] The size of the obtained nanoparticles was limited to 15 nm, with a narrow distribution. The gold nanoparticles are stable in the dispersion, maintaining their morphology during several months.[65] An important characteristic of this dispersion is its ability to be evaporated, forming a very stable powder system, which can be stored for several months and easily transported. The nanoparticles powder can be redispersed in water, due to the solubility afforded by the ionic groups, maintaining their morphological and optical properties. This feature allows easy handling enabling their use as a source of nanoparticles for the preparation of several other systems in the form of powder, films, monoliths and others, as depicted in Figure 3. It is valid to highlight that in all of these systems the accessibility to the metal nanoparticles

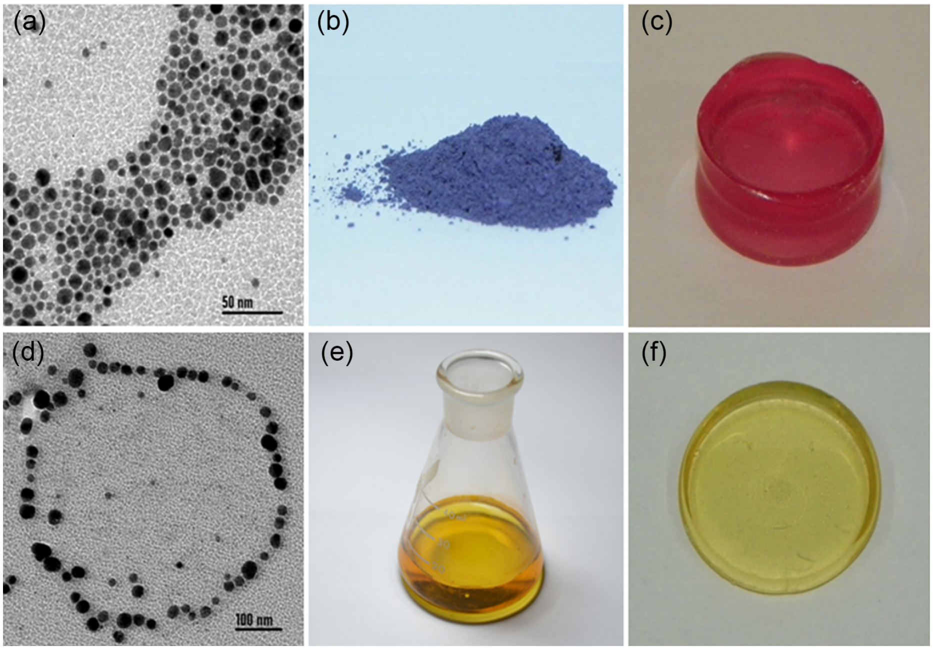


Figure 3. Images of gold and silver nanoparticles stabilized by ionic silsesquioxane: (a) TEM images of gold nanoparticles; (b) picture of gold nanoparticles in the powder form; (c) silica monolith doped with gold nanoparticles; (d) TEM images of silver nanoparticles; (e) silver nanoparticle aqueous dispersion; (f) silica monolith doped with silver nanoparticles.

were maintained, warranting the application as catalysts, antimicrobial agent, electroactive species for sensors, etc.

Water soluble pendant silsesquioxanes containing pyridinium, picolinium and amino-methyl-pyridinium were also prepared by other research groups, by using two step synthesis.[66-68] These ionic silsesquioxanes were used to stabilize gold, silver and palladium nanoparticles that were applied in the development of electrochemical devices.

5. Ionic Silsesquioxanes for Designing Nanomaterials and Nanodevices

5.1. Exploring the ion-exchange capacity to prepare hydrophobic silsesquioxanes to input specific properties to surfaces, films and bulk materials

Using the ion-exchange properties, the counter ion chloride of the bridged ionic silsesquioxane that contains the 1,4-diazoniabicyclo[2.2.2]octane group was exchanged by the stearate. As this anion presents an 18-carbon alkyl chain, it affords hydrophobicity to the ionic silsesquioxane hybrid polymer, in this way it can act as surfactant, opening possibilities to architect new materials.[40] As an example, the hydrophobic silsesquioxane was used to disperse nonpolar multiwalled carbon nanotubes (MWCNT) in low dielectric constant solvents such as butyl alcohol. The dispersion involves molecular interactions of the 18 carbon chain with the MWCNT and butyl alcohol. This dispersion was applied to prepare ceramic matrices like zirconia and alumina containing very dispersed MWCNT, by using sol-gel synthesis method. Besides, a very good interface between MWCNT and ceramic matrices was attained, enabling MWCNT to promote the reinforcement of the ceramic matrices.[40] This interaction is based on the adsorption of the stearate long carbon chain along the hydrophobic MWCNT surface, and the Si–O component that makes covalent bonds to the aluminum or zirconium of ceramic oxide moiety, as depicted in Figure 4, along with scanning electron microscopy (SEM) images. In this way, the possibility to prepare new reinforced and well dispersed MWCNT/ceramic nanocomposites was proposed.

Applying a similar method, where the same interactions are established, hydrophobic silsesquioxane was dissolved in butyl alcohol and used to disperse magnetic Fe-decorated MWCNT. In sequence, the system was used to prepare magnetic thin films over small, polished silicon substrates and glass slides.[69] The sol-gel method and dip-coating technique were applied as deposition techniques promoting a good dispersion of MWCNT. Profilometry measurements for films planned to have 0.5% by weight of nanotubes show 173 ± 5 nm thickness. The magnetic properties of the films, by using alternating gradient-field magnetometer measurements, showed a coercivity of 103 Oe. Based on this high magnetic response, it can be proposed that this

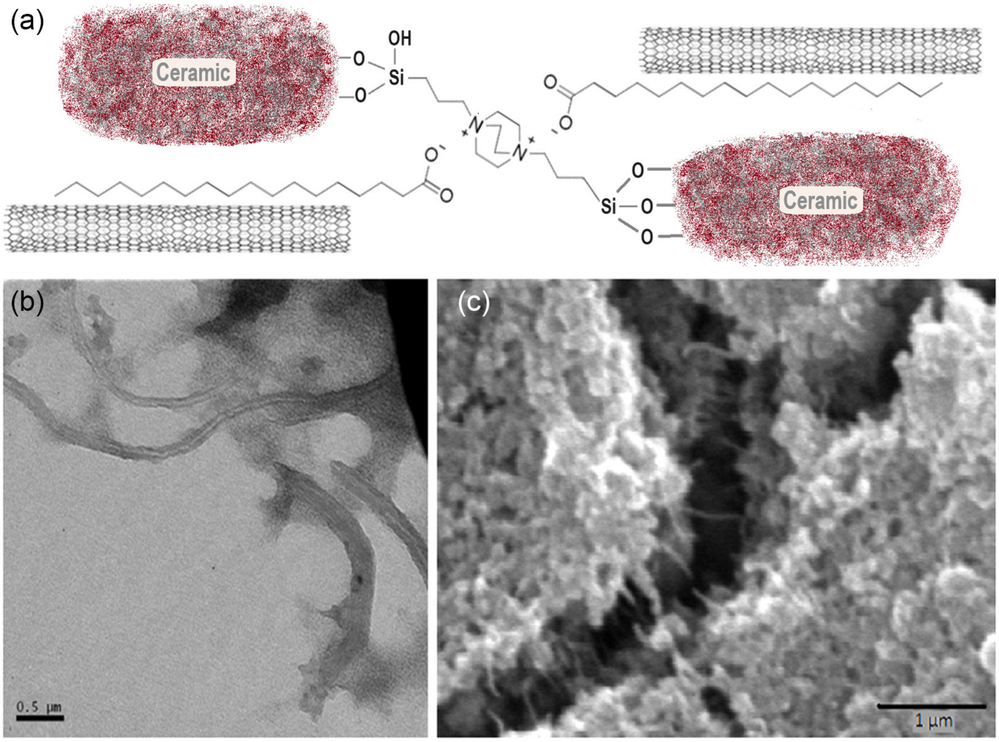


Figure 4. (a) Schematic representation of silsesquioxane interacting with both the MWCNT and the ceramic oxide matrix; (b) TEM and (c) SEM images of MWCNT dispersed in zirconia oxide ceramic.

composite film has a potential application for magnetic storage devices.

The hydrophobic silsesquioxane was also applied in the immobilization of *Thermomyces lanuginosus* (TLL) enzyme inside of the mesopores of magnetic silica support, obtained by sol-gel method.[70] In that report, firstly submicrometric magnetite particles were synthesized and embedded in a mesoporous silica xerogel. This magnetic material was planned to present pore size adequate for the TLL enzyme immobilization. In sequence, the hydrophobic silsesquioxane was grafted on the material surface, due to the capacity of forming films over the silica surface, stabilized by the Si–O–Si bonds. The resulting modified material showed a hydrophobic surface, with a water drop contact angle of 125°. The high hydrophobicity of the surface provided a higher amount of adsorbed TLL enzyme and a better preservation of its activity when compared to the hydrophilic one. Additionally, the embedded magnetite provided magnetic recovery of material enabling recyclability of the biocatalyst in the model reaction of *p*-nitrophenyl palmitate hydrolysis.

5.2. Development of very stable nanostructures for antimicrobial systems

The control of microbial activity is becoming more important in each decade, mainly due to the resistance to antibiotics that was developed by the microorganisms.[71] In this context, the silsesquioxanes containing quaternary ammonium groups and applied to stabilize the metal nanoparticles arise as a promising alternative. The quaternary ammonium groups are well known for their inhibitory and antimicrobial effects.[72] Our group reported[73] the first use of an ionic silsesquioxane as an antimicrobial system. In this report the silsesquioxane containing quaternary ammonium groups and nitrate as counter ions was synthesized and applied as stabilizer and size controller of silver nanoparticles. The ion chloride exchange by nitrate was very important because the presence of the chloride can cause precipitation of silver chloride hindering the metal nanoparticles formation. The aqueous dispersion of very small, 5 nm average diameter silver nanoparticles, with high morphological stability, presented the best antibacterial activity against *S. aureus*, 0.6 μg mL^{-1} of silver in the nanoparticle form.[73] The cytotoxicity for mammalian cells was tested showing that the silver nanoparticles are safe at the studied silver grade.

The same ionic silsesquioxane containing nitrate as a counterion was used to plan thin films containing spherical silver nanoparticles (diameter lower than 10 nm) on flat glass surfaces,[74] as represented in Figure 5. The films were manufactured without previous treatment or functionalization of the glasses, and even so, they showed high thermal stability up to 200 °C, maintaining their

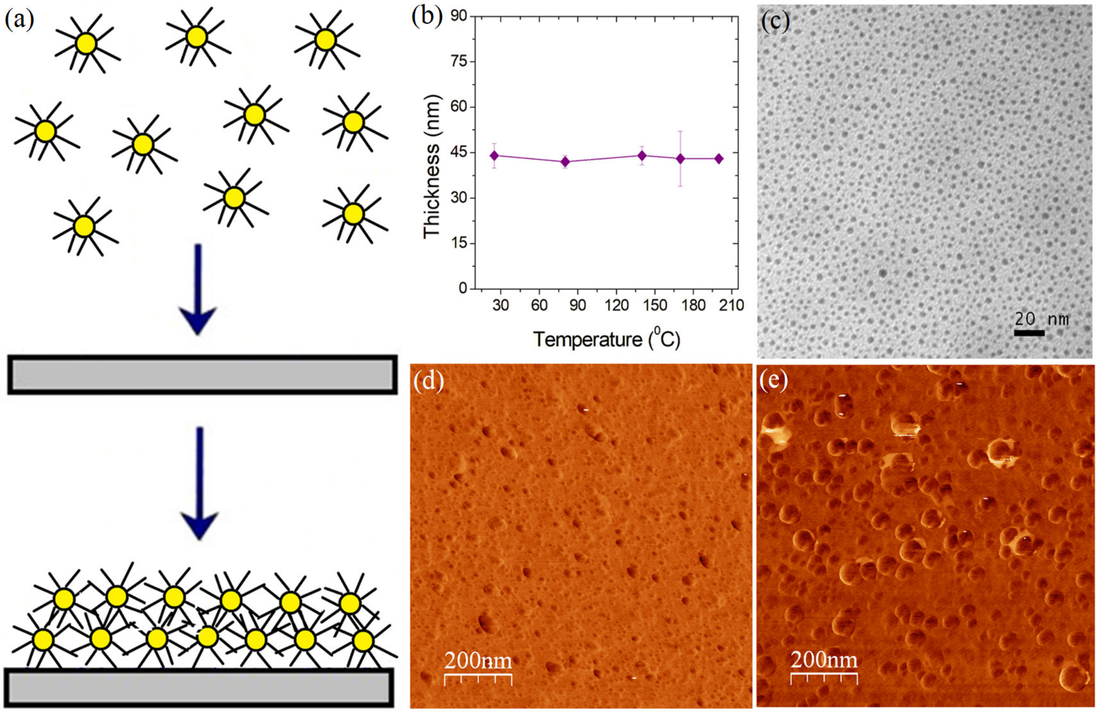


Figure 5. Silver nanoparticle films on glass surfaces: (a) schematic representation of the film formation; (b) film thickness obtained by ellipsometry; (c) TEM image of the silver nanoparticle films; (d) phase contrast images obtained by AFM for silver nanoparticle films (room temperature) and (e) heat treated up to 200 °C (Figure 5 reproduced from reference 74 with copyright permission from SBQ).

thicknesses constant. Figure 5 also shows atomic force microscopy (AFM) images of the films. The stability of the films is due to the covalent bond established between the Si–O groups of the silsesquioxane and the Si atoms of the glass surface as already presented in "3.2. Water solubility and adhesion to metal oxide surfaces" sub-section. Also the embedded silver nanoparticles preserved their morphological and optical characteristics upon heating. The films presented great antimicrobial activity, even after several thermal sterilization cycles, making them very promising to be applied in hospital materials. The excellent activity was interpreted taking into account the synergic effect of the silver nanoparticles and the quaternary ammonium groups of the ionic silsesquioxane.[74]

In a similar procedure used to prepare silver nanostructures, gold nanoparticles stabilized by ionic silsesquioxane were also applied as antimicrobial agents.[75] The gold nanoparticles were incorporated in biodegradable films of quinoa starch improving the mechanical properties and affording high thermal stability, up to 270 °C. Also, the presence of the gold nanoparticles provides great antimicrobial activity to the films, showing inhibition percentages of 99% against *E. coli* and 98% against *S. aureus* bacteria. The obtained results make this system very promising to be applied in active food packages.[75]

5.3. Architecting efficient nanocatalysts for organic synthesis

The development of heterogeneous catalysts has advanced substantially in recent years due to the success in developing new nanostructured materials, which include supports with ordered pore structure as well as very active nanoscale catalysts.[45,46,76] These nanocatalysts include supported nanoparticles, clusters and even single atom species.[46,77,78] They present high surface area and low cost, since they are obtained using a low amount of metal precursors, making the process more efficient and environmentally friendly. In this context, the ionic silsesquioxanes are very promising to be applied in the design of these new catalysts, since besides being a stabilizer and size controller of metal nanoparticles, they can work also as adhesion agents on inorganic surfaces, due to the Si–O covalent bonds that can be performed with Si or metals such as Al, Zr, Ti, as already explained.[65,74] In this way, they can be used to produce metal nanoparticles or other nanocatalysts strongly adhered into the pores of inorganic supports. As the ionic silsesquioxanes can be grafted onto the pore surface, they generate ionic sites to adsorb anionic metal complexes, such as $AuCl_4^-$, $PtCl_4^{2-}$ or $PdCl_4^{2-}$ through an ionic exchange process. Different from the covalent bonds, the ionic interactions are multidirectional and allow a long range effect. Thus, they can be used to produce atomic dispersions of these metal ion complexes, which work as precursors for metal nanoparticles synthesis. These highly dispersed ions act as nucleation sites during the chemical reduction synthesis. Therefore, the use of ionic silsesquioxanes leads to the formation of small metal nanoparticles, without significant changes in the textural characteristics of the support, as surface area and pore size distribution.[79] Using this strategy, we have shown that it is possible to insert small gold nanoparticles inside the ordered pores of SBA-15 (Santa Barbara amorphous, number 15) type material. The obtained material was successfully applied as a catalyst, using only 0.6 mol% of gold, in the synthesis of 2-aryl-2,3-dihydroquinazolin-4(1*H*)-ones, which are recognized as a base structure for medicine synthesis.[80] Typical images of gold nanoparticles synthesized inside of the SBA-15 pores are depicted in Figure 6.

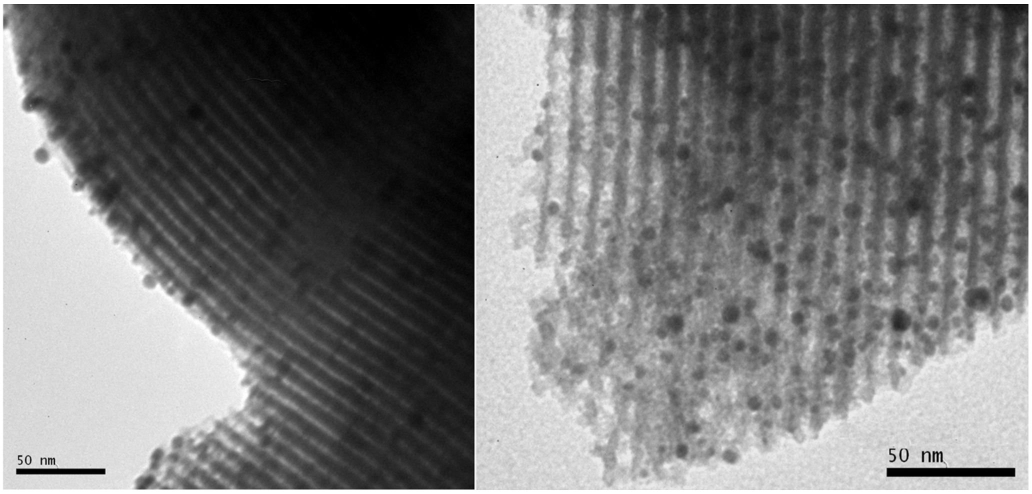


Figure 6. TEM images of highly ordered mesoporous SBA-15 silica material decorated with gold nanoparticles.

In another paper[81] we have reported the use of $AuCl_4^-$ complex anchored to porous silica matrix modified with ionic silsesquioxane which was applied as catalyst for cross coupling reactions to obtain symmetric and non-symmetric 1,3-diynes, using just 0.22 mol% of Au^{III} catalyst. In this paper, the offered quantity of Au^{III} complex was just 12% of the available cationic sites. This small amount of gold complex provides isolated sites on the silica surface, hindering the metal aggregation which could harm the atomic dispersion, and therefore, keeping the Au^{III} as available sites for the catalysis.[81]

5.4. Developing electrochemical sensors for environmental and health applications

Exploring the ion-exchange properties, the ability to stabilize metal nanoparticles and also the capability to adhere covalently on inorganic surfaces, the ionic silsesquioxanes have been used in the manufacture of several electrochemical sensors for analytical applications.[82-84] Using the ion-exchange capacity, we have demonstrated that ionic silsesquioxane that contains the 1,4-diazoniabicyclo[2.2.2]octane grafted onto the silica surface can adsorb electroactive species as copper tetrasulfonated phthalocyanine. This material was used to manufacture carbon paste electrodes that showed excellent electrochemical response to the dopamine redox process.[39] Similar metal phthalocyanine species were also adsorbed in silsesquioxanes containing pyridinium and picolinium group, and they were employed in the oxalic acid[85] and sulfanilamide[35] quantification. Based on the ability to stabilize metal nanoparticles, the ionic silsesquioxanes containing pyridinium and the 1-azonia-4-azabicyclo[2.2.2]octane pendant groups were used to produce gold nanoparticles smaller than 10 nm of diameter, which were immobilized on the surface of silica grafted with aluminum oxide. The presence of these gold nanoparticles improved the electrochemical response of these modified carbon paste electrodes, when applied in the nitrite determination.[86] Also, SBA-15 material decorated with silver nanoparticles stabilized by the ionic silsesquioxane that contains the 1,4-diazoniabicyclo[2.2.2]octane bridged group was successfully applied in the simultaneous determination of paracetamol and sulfamethoxazole medicines.[87] Other research groups[66-68,88,89] developed electrochemical sensors and biosensors containing metal nanoparticles, such as silver, gold and palladium nanoparticles stabilized by ionic silsesquioxanes for application in health area.

Aiming to obtain metal nanoparticle enriched silica materials, to be applied in the manufacture of electrodes, another interesting strategy was reported. The strategy involves the *in situ* synthesis of the metal nanoparticles inside of the pores. For this purpose, the silica surface was previously grafted with ionic silsesquioxane, and the cationic groups worked as adsorbent sites for anion metal complexes, which undergo chemical reduction to form the metal nanoparticles strongly adhered on the silica surface. This strategy was used to obtain gold nanoparticles on hybrid xerogel containing silica and 3-(1-imidazolyl)propyl silsesquioxane. The material was applied in the manufacture of modified carbon paste electrodes, which were used in the 4-nitrophenol determination.[90] More recently, a similar strategy was applied to obtain silver nanoparticles confined inside of the ordered SBA-15 pore structure.[91] In this report, we have firstly synthesized the anion complex $Ag(CN)_2^-$, which was adsorbed on the SBA-15 surface, previously grafted with ionic silsesquioxane. The adsorbed complex ions remain highly dispersed on the surface, and they were used as sites for silver nanoparticles nucleation and growing. The resulting SBA-15 material decorated with silver nanoparticles was successfully applied in the electrochemical amoxicillin determination, even in real samples.[91] It is important to highlight that in all the developed sensors, the metal nanoparticles stabilized by ionic silsesquioxanes play an important role, improving the electrochemical response and the sensibility of the electrodes.

5.5. Designing nanodevices for generation of sustainable energy

The ionic silsesquioxanes developed by our research group have been also used in the renewable energy field. Using the ability to obtain solid metal nanoparticles, gold nanospheres in the powder form were applied to improve the photocurrent in organic solar cell assembly.[92] Nevertheless, perhaps the paper that better describes the versatility of the ionic silsesquioxanes in the architecture of nanodevices was reported in 2019.[93] In that paper, all the ionic silsesquioxane properties were explored, allowing it to play several roles. It was explored the ability to stabilize metal nanoparticles, the water solubility property and the capability to adhere strongly on inorganic surfaces. The ionic silsesquioxane that contains the bridged 1,4-diazoniabicyclo[2.2.2]octane group was used to obtain anatase nanotubes with high surface area ($350\ m^2\ g^{-1}$) and decorated with small gold nanoparticles (lower than 10 nm). Therefore, the ionic silsesquioxane worked as an anti-sintering agent of anatase, preserving its nanotubular morphology, even after the calcination at 450 °C. Also, the gold nanoparticles morphology was preserved during the thermal treatment. The schematic synthesis procedure, as well as a TEM image of the material, are depicted in Figure 7. This robust material was successfully applied as a photocatalyst for hydrogen production by water splitting. Successive cycles of 5 h in the water splitting reactor were performed and the photocatalytic activity of the anatase nanotubes decorated with gold nanoparticles, in the hydrogen generation was about 5 times superior than anatase nanotubes and 20 times higher than the activity of the commercial titanium oxide powder P-25® Degussa.[93] This excellent performance was interpreted considering the synergistic two ways. The first, the silica coating hinders the titania grain growth and sintering, maintaining its nanotubular morphology with high surface area. The second one is due to the presence of gold nanoparticles, which enlarge the spectral absorption range, leading to the formation of "hot electrons" that are injected in the conduction band of anatase.[94]

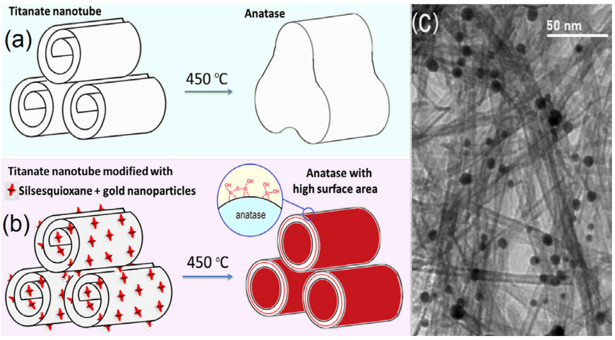


Figure 7. Schematic representation of the anatase nanotube preparation; (a) pure anatase nanotube; (b) anatase nanotubes decorated with gold nanoparticles; (c) TEM image of anatase nanotubes decorated with gold nanoparticles.

6. Conclusions

Due to the peculiar features of the ionic silsesquioxanes, such as structural self-organization, ion-exchange property, solubility in solvents with high dielectric constant, capability to form stable films strong adhered to inorganic surfaces and the ability to stabilize metal nanoparticles, these ionic hybrid polymers emerge as versatile tools to architect innovative nanostructured materials as well as to develop nanodevices. We have shared here that the ionic silsesquioxanes were successfully applied in the development of (*i*) nanocomposite ceramics, which contain highly dispersed carbon nanotube, aiming to improve the ceramic toughness; (*ii*) very efficient antimicrobial systems containing metal nanoparticles as suspensions, as films on flat surfaces or even embedded in biodegradable food package; (*iii*) high performance nanocatalyst for organic synthesis; (*iv*) highly sensible electrochemical sensors for detection and quantification of environmental and biomedical species; (*v*) very active photocatalyst in the hydrogen generation by water splitting, among other applications.

Therefore, taking into account the versatility of ionic silsesquioxanes that can be handled in varied configurations, such as aqueous dispersions, powders, films and monoliths, allied to their physico-chemical features, we believe that ionic silsesquioxanes constitute important tools to design innovative nanostructures and new nanodevices for several areas that can attend the future demands of the humanity, highlighting health, energy and sustainability.

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