



Macromolecular Nanotechnology

Synthesis and characterization of a nanostructured photoluminescent silsesquioxane containing urea and dodecyl groups that can be patterned on carbon films

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ABSTRACT

A silsesquioxane was synthesized by the hydrolysis and polycondensation of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHCONH}(\text{CH}_2)_{11}\text{CH}_3$ in tetrahydrofuran (THF) employing formic acid as catalyst. The silsesquioxane self-assembled into nanorods due to the strong H-bonds among urea groups and the tail-to-tail associations of organic chains. The nanostructuration was characterized by a variety of experimental techniques (FTIR, ^{29}Si NMR, XRD, TEM, HRTEM, and SAED). A colloidal solution of the silsesquioxane in methanol was deposited on a carbon film generating coffee ring structures with nanoparticles located at the boundary of rings. The significance of these results is related to the intrinsic photoluminescence of silsesquioxanes containing urea groups. The possibility of patterning these hybrid polymers on a surface can give place to materials exhibiting periodically modulated optical properties with potential applications in optoelectronics and light-emitting devices.

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1. Introduction

Polymers with specific properties (optical, electric, magnetic, etc.) can be patterned on surfaces using ink-jet printing, soft lithography, screen printing, reactive patterning, and related techniques, to produce functional materials and devices for different applications [1–4]. Patterned films with periodically modulated optical properties find applications in optoelectronics and light-emitting devices [5–7]. In this article we report the patterning of a photoluminescent silsesquioxane synthesized by the hydrolysis and condensation of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHCONH}(\text{CH}_2)_{11}\text{CH}_3$. Silsesquioxanes containing substituted urea groups, $-\text{NH}-\text{CO}-\text{NH}-$, exhibit intrinsic photoluminescence arising from electron–hole recombinations in the inorganic

domains (purplish-blue band) and photoinduced proton-transfer between urea groups convoluted with the emission from the inorganic clusters (blue band) [8–18]. In particular, a bridged silsesquioxane with a similar chemical structure to the one used in this study [19,20], showed photoluminescence in the visible region [21].

The process selected to generate a patterned surface was the self-assembly of nanoparticles produced during the deposition of a colloidal solution of the silsesquioxane on an adequate surface. The first condition to fulfill this requirement was to synthesize silsesquioxane nanoparticles that could be temporarily stabilized as a colloidal dispersion in a convenient solvent. The chemical structure of the selected precursor enabled the generation of nanoparticles by the self-assembly produced by strong H-bonds among urea groups and tail-to-tail association of organic chains. The dispersion of these nanoparticles in methanol provided the colloidal solution employed for the patterning. The second condition required to produce the desired patterning was to select a surface that was

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not wetted by methanol. A carbon film was successfully employed. Dip-coating carbon films with the colloidal solution of the silsesquioxane produced a dispersion of micron-size droplets by dewetting of the solvent. During the drying step, the capillary flow towards the pinning line produced coffee-ring structures [22–24], with silsesquioxane nanoparticles located at the boundaries of the rings. The process might be adapted to a conventional ink-jet printing technique to obtain a patterned photoluminescent film.

The synthesis and characterization of the precursor, the nanostructured silsesquioxane and the patterned carbon films are consecutively analyzed.

2. Experimental section

2.1. Synthesis of the precursor

The precursor $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHCONH}(\text{CH}_2)_{11}\text{CH}_3$ was synthesized as follows: 10 mmol of dodecylamine (DA, Acros Organics, USA, 98% purity) were dissolved in 30 ml dehydrated tetrahydrofuran (THF) with stirring, and 10 mmol of (3-isocyanatopropyl) triethoxysilane (IPTES, Tokyo Chemical Industry, 95% purity) were slowly added. The recipient was sealed with a plastic film and heated at 55 °C in a water-bath for 6 h.

2.2. Synthesis of the colloidal solution of the silsesquioxane

Needle-size holes were made on the plastic cover of the recipient containing the THF solution of the precursor. Temperature was decreased to 39 °C and 2 ml distilled water and 0.15 ml of a formic acid solution (1.5 M), were added. The hydrolysis and condensation of the precursor took place together with a slow evaporation of volatiles. After about 8 h, a pale-yellow colloidal solution was obtained which remained stable for approximately 4 h. After about 12 h of the beginning of the synthesis, the silsesquioxane began to precipitate. The silsesquioxane nanoparticles present in the colloidal solution were observed by dip-coating glass covers with this solution and drying at room temperature. A fraction of the solution was stored at 39 °C enabling complete evaporation of volatiles. The silsesquioxane present as a powder was analyzed employing different techniques.

2.3. Patterning on a carbon film

The colloidal solution obtained after 8 h condensation was diluted with methanol (100:1 volume ratio) and dip-coated on a TEM support covered by an ultra-thin carbon film (3–5 nm thickness) (Allied High Tech Products, USA). Coffee ring structures were spontaneously formed when drying the colloidal solution at room temperature.

2.4. Characterization techniques

FTIR spectra were obtained with a Nicolet Avatar 360 FTIR device. Electrospray ionization mass spectrometry (ESI-MS) was performed with an Agilent 1100 LC-

MSD-Trap-VL system in the positive ion mode. TEM and HRTEM images were obtained with a Philips-FEI Tecnai G2 F30 device, operating at 300 kV. The instrument was provided with a SAED (selected area electron diffraction) technique. Small-angle X-ray diffraction spectra were obtained with a Philips X'Pert diffractometer employing $\text{Cu-K}\alpha$ radiation generated at 40 kV and 40 mA. A Göbel mirror was used to obtain parallel X-rays. ^{29}Si { ^1H } CP/MAS spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 7 mm standard bore CP/MAS probehead whose X channel was tuned to 79.50 MHz for ^{29}Si and the other channel was tuned to 400.18 MHz for broadband ^1H decoupling. The dried and finely powdered samples were packed in the ZrO_2 rotor closed with Kel-F cap. The spun rate was 5 kHz. A total of 1400 scans were recorded with 60 s recycle delay for each sample. ^{29}Si CP/MAS chemical shifts were referenced to the resonances of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) standard ($d = 0.0$).

3. Results and discussion

3.1. Characterization of the precursor

The precursor synthesized by the reaction of equimolar amounts of (3-isocyanatopropyl) triethoxysilane and dodecylamine was characterized by ESI-MS and FTIR. Fig. 1 shows the mass spectrum of the precursor. The main peak at 455.1 Da corresponds exactly to the mass of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHCONH}(\text{CH}_2)_{11}\text{CH}_3$ ionized with Na^+ . The peak at 433.0 Da indicates the mass of the precursor ionized with H^+ . The other intense peak at 387.1 Da corresponds to the mass of the fragment $(\text{EtO})_2\text{-Si}^+(\text{CH}_2)_3\text{NHCONH}(\text{CH}_2)_{11}\text{CH}_3$ produced by the loss of an EtO^- anion from the precursor during the electro-spray ionization.

The FTIR spectrum showed the absence of the NCO band at 2274 cm^{-1} indicating that the reaction was complete. Characteristic bands of the urea group were present at 1580 cm^{-1} (amide II) and 1633 cm^{-1} (amide I). A broad-band with a maximum at 1080.7 cm^{-1} (Si–C) showed a superimposed band at about 957 cm^{-1} characteristic of Si–OEt groups. There was no band at 910 cm^{-1} expected for SiOH groups, indicating that spurious hydrolysis of ethoxysilane groups did not occur. Both ESI-MS and FTIR characterization evidenced that the synthesis of the precursor was carried out to completion.

3.2. Characterization of the nanostructured silsesquioxane

The colloidal solution of the silsesquioxane obtained after 8 h condensation was dip-coated on a glass cover obtaining a thin film. TEM images (Fig. 2) showed the presence of nanoparticles with a broad distribution of sizes, dispersed in a continuous matrix. The high-resolution image revealed the presence of domains with a regular structure inside the nanoparticles.

The silsesquioxane obtained after complete evaporation of the solvent was analyzed by FTIR and ^{29}Si NMR, obtaining an average characterization of organized and

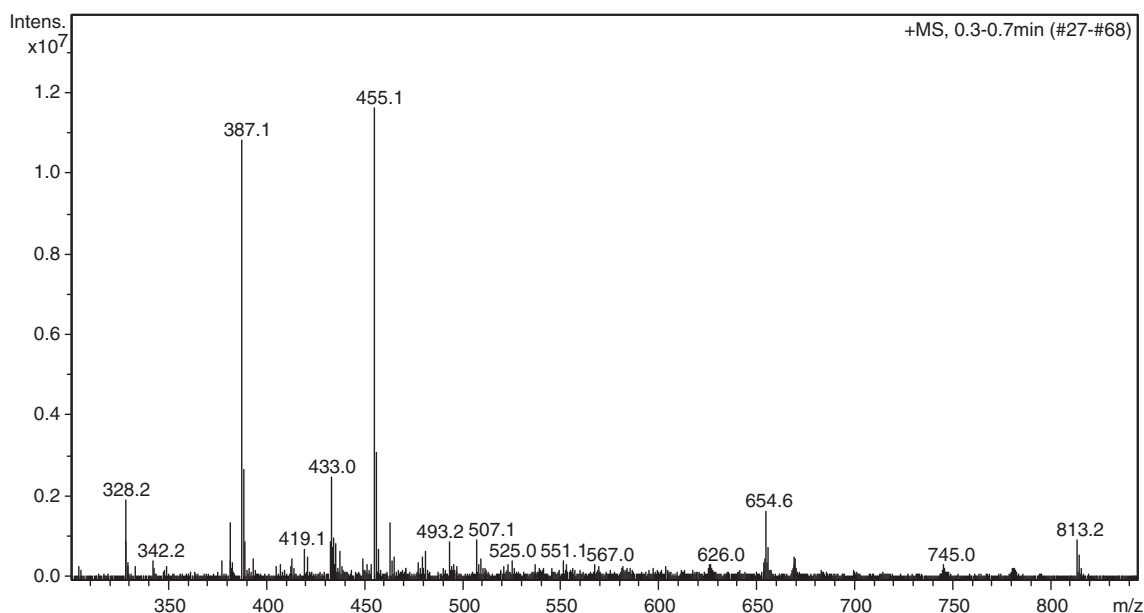


Fig. 1. ESI-MS of the precursor.

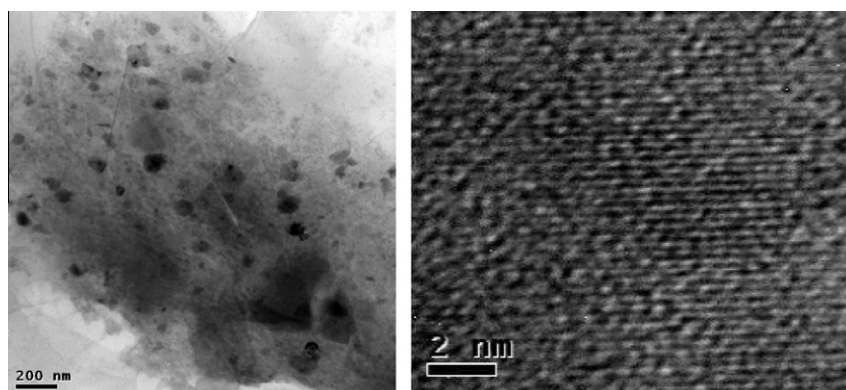


Fig. 2. TEM and HRTEM images of the film made by dip-coating the colloidal solution of the silsesquioxane on a glass cover.

amorphous domains. The FTIR spectrum of the resulting product is shown in Fig. 3. The frequencies of the methylene symmetric (d^+) and antisymmetric (d^-) stretching vibrations are sensitive to the conformation of alkyl chains. For all-trans (extended) chains d^+ is in the range of $2846\text{--}2850\text{ cm}^{-1}$ and d^- is between 2918 and 2919 cm^{-1} [25]. These values are respectively shifted to 2856 and 2928 cm^{-1} for chains with trans-gauche conformations (disordered chains) [25]. The experimental values shown in Fig. 3 are, respectively, 2851 and 2921 cm^{-1} , indicating that dodecyl chains have conformations close to the fully extended condition. The strength of the H-bonds among urea groups can be characterized by the difference in frequencies between amide I (ν_{CO} close to 1650 cm^{-1}) and amide II bands (δ_{NH} close to 1570 cm^{-1}). The difference between both frequencies ($\Delta\nu$) decreases when increasing the strength of the H-bonds [19,26]. In the absence of H-bonding, $\Delta\nu = 120\text{ cm}^{-1}$ and the value

decreases to about $30\text{--}50\text{ cm}^{-1}$ when strong H-bonds are formed [19,26]. In our case, Fig. 3 shows $\Delta\nu = 37\text{ cm}^{-1}$ confirming the presence of very strong H-bonds among urea groups. Another proof of the presence of very strong H-bonds is the location of the NH band at 3339 cm^{-1} [19]. Another interesting feature of the FTIR spectrum is the unusual location of the band assigned to the Si—O—Si antisymmetric stretching mode. In our case the main band corresponding to this mode is located at 1022 cm^{-1} . A characteristic single band at 1020 cm^{-1} is found in trimers: $[\text{RSiO}(\text{OH})_3]$ with strained O—Si—O angles [27]. This can be interpreted by the fact that the strong H-bonds among urea groups determined a strained structure of the inorganic layer. The band at 910 cm^{-1} , assigned to SiOH groups, indicates a partial condensation of the silsesquioxane.

The ^{29}Si NMR CP/MAS spectrum (Fig. 4) revealed the presence of two peaks at -60.66 ppm , assigned to

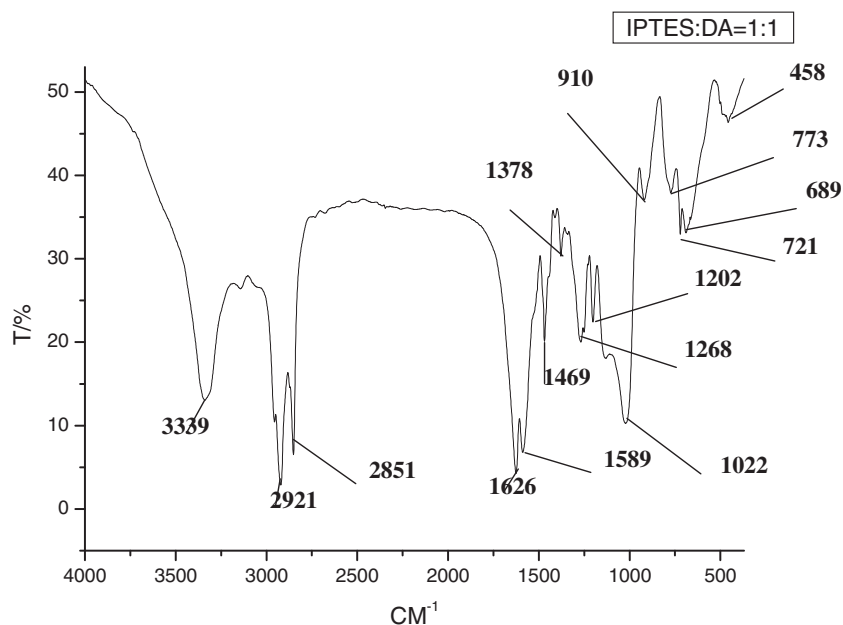


Fig. 3. FTIR spectrum of the nanostructured silsesquioxane.

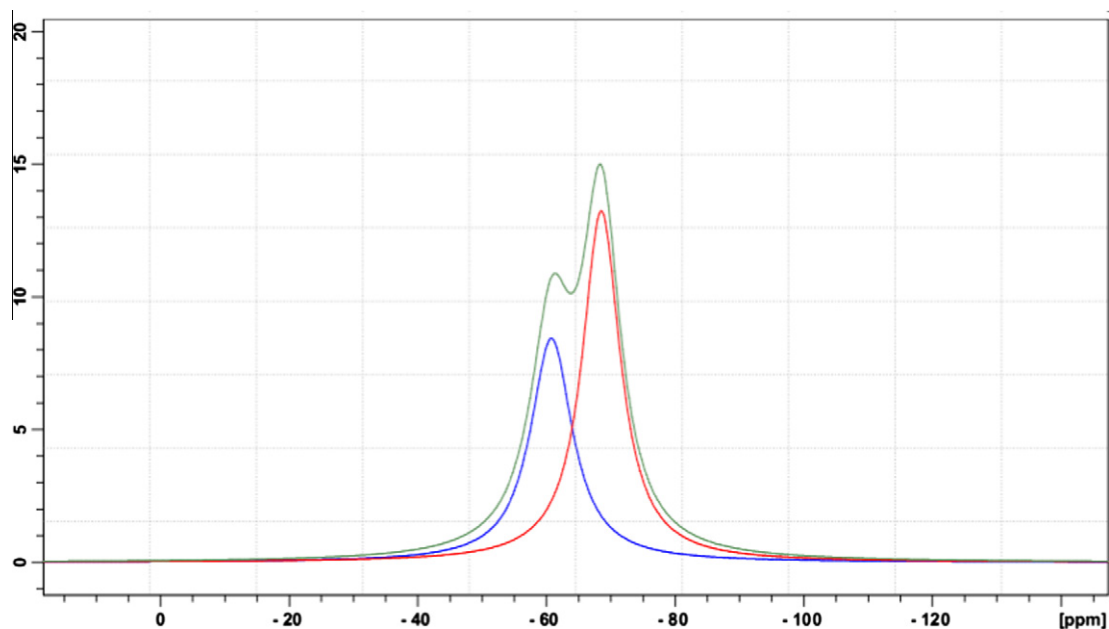


Fig. 4. ^{29}Si NMR CP/MAS spectrum of the nanostructured silsesquioxane.

$\text{RSiO}_2(\text{OH})$ structures (T_2), and at -68.39 ppm, assigned to RSiO_3 (T_3) structures. No T_0 or T_1 structures were present in the spectrum. A precise quantification of the fraction of T_2 and T_3 structures would have required using a single pulse sequence rather than CP/MAS.

A small-angle X-ray diffraction spectrum (Fig. 5) of the film made by dip-coating the colloidal solution of the silsesquioxane on a glass cover, revealed the presence of a narrow peak at $2\theta = 2.97^\circ$, corresponding to a

characteristic distance $d = 3.0$ nm. The length of the extended organic group was estimated as 2.4 nm, meaning that the nanostructuring of the silsesquioxane must arise from the tail-to-tail association of organic groups issuing from neighboring inorganic layers. The tail-to-tail association of alkyl chains has been reported as a mechanism leading to the generation of organized structures in different types of silsesquioxanes [28–31]. The characteristic distance observed in our case would require a non-

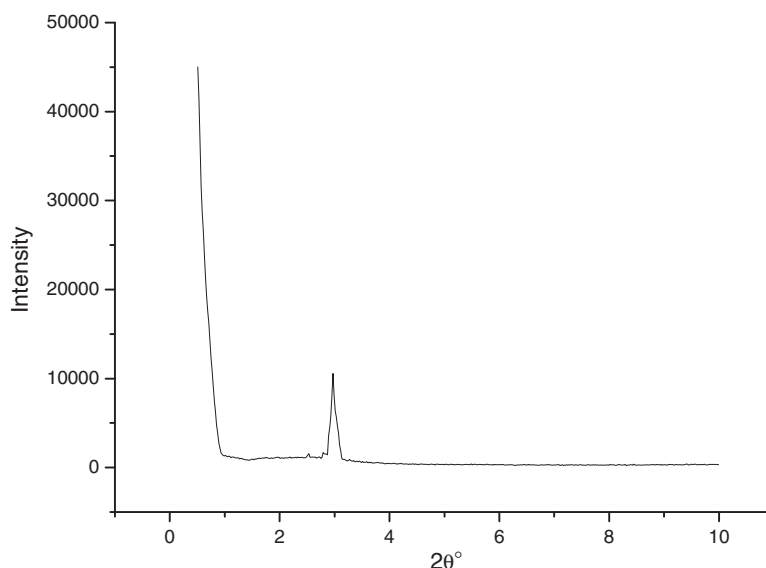


Fig. 5. Small-angle X-ray diffraction spectrum of the film made by dip-coating the colloidal solution of the silsesquioxane on a glass cover.

perpendicular (tilting) or a non-extended conformation of the organic group, or the interdigitation of dodecyl chains [31].

It is interesting to point out that the observed characteristic length (3.0 nm) is practically the same as the one reported for the organic group $R = (\text{CH}_2)_3\text{NHCONH}-(\text{CH}_2)_{12}\text{NHCONH}(\text{CH}_2)_3$, separating Si atoms located in neighboring inorganic layers of a bridged silsesquioxane [19–21]. For our case, this means that if the organic chains are completely extended, full interdigitation of dodecyl chains would be required to account for the observed characteristic length.

The tail-to-tail association of organic chains issuing from neighboring inorganic layers generates a lamellar structure [28,31]. The correlation length (ζ) related to the structural order range of the lamellar structure may be calculated as: $\zeta = 2\pi/\Delta q$, where Δq is the width of the scattering peak expressed in scattering vector units, $q = (4\pi/\lambda) \sin\theta$, and measured at half maximum [20]; λ is the wavelength of the Cu-K α radiation. The resulting value was $\zeta = 737$ Å, meaning that the order extends to about 25 interlayer distances, a fact that is qualitatively reflected by the sharpness of the diffraction peak.

3.3. Coffee ring patterns on carbon films

The colloidal solution of the silsesquioxane obtained after 8 h condensation was diluted with methanol (100:1 volume ratio) and dip-coated on ultra-thin carbon film (3–5 nm thickness). Coffee ring structures were spontaneously formed by a combination of dewetting of the liquid film and induced capillary flow towards the pinning line (Fig. 6). Most rings have diameters in the range of 0.5–2.5 μm with a rim thickness/diameter ratio close to 1:10. Silsesquioxane nanoparticles with sizes in the range of 50–200 nm are present at the boundary of rings.

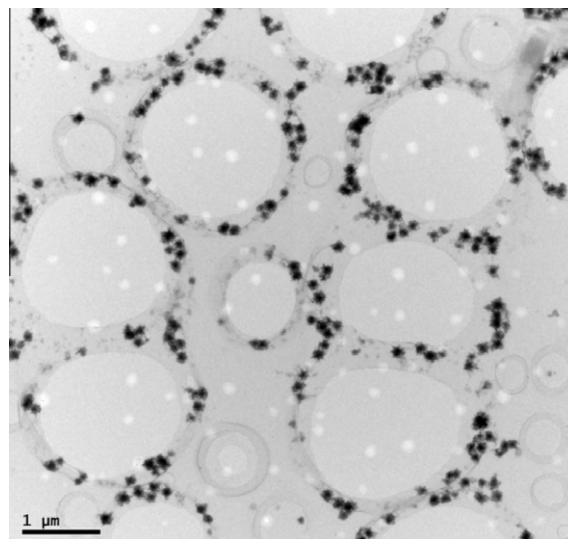


Fig. 6. TEM image of coffee-ring structures formed by silsesquioxane nanoparticles on the surface of carbon films.

TEM and HRTEM images with different magnifications (Fig. 7) show that silsesquioxane nanoparticles are composed by a dispersion of crystalline nanorods issuing from an amorphous matrix. The nanorods exhibit an irregular boundary with an average diameter close to 8 nm and lengths in the range of 50–100 nm. The average length of nanorods lies in the same range than the correlation length of the lamellar structure ($\zeta = 74$ nm). Therefore, we may assume that nanorods are formed by a lamellar structure produced by the tail-to-tail association of organic chains located in neighboring inorganic layers.

The structure of the inorganic layer was investigated by SAED of a crystalline nanorod (Fig. 8). A series of five concentric rings reveals the presence of a polycrystalline

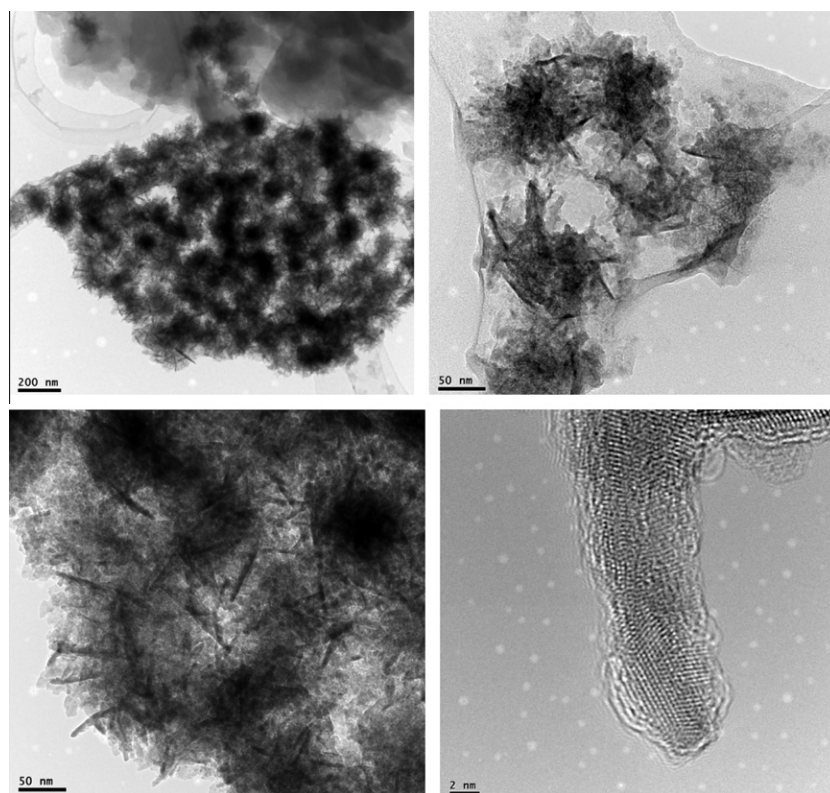


Fig. 7. TEM and HRTEM images with different magnifications showing the structure of silsesquioxane nanoparticles located at the boundaries of rings.

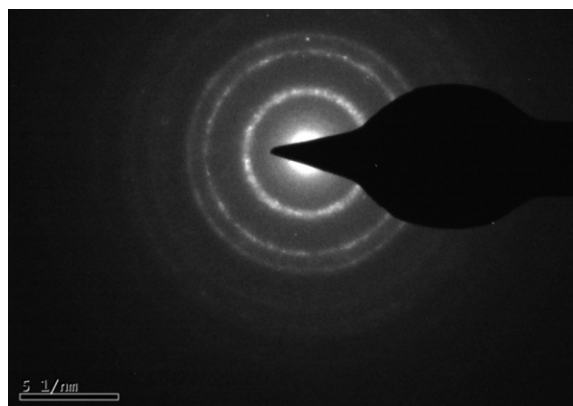


Fig. 8. SAED spectrum of the crystalline structure of a nanorod.

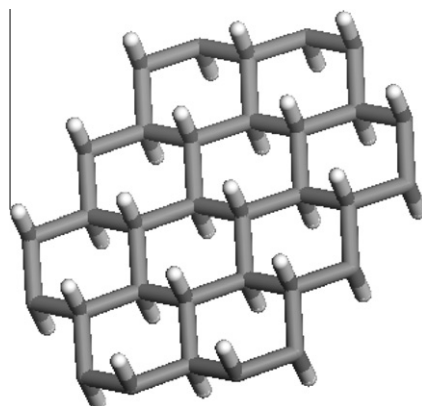


Fig. 9. Proposed 2D hexagonal structure of the inorganic layer.

structure. The radii of concentric rings followed the proportions: $1:3^{1/2}:2:7^{1/2}:3$, associated with a 2D hexagonal structure [32]. The characteristic distance, d_{10} , calculated from the location of the first ring was 3.4 Å. Fig. 9 shows the proposed scheme for the 2D hexagonal structure of the inorganic layer. Si atoms are located at every vertex of the hexagon bonding three other Si atoms (Si–O–Si bonds) and the organic group (R); O atoms (not shown) are located in the sides of the hexagons bonding two Si atoms. The organic groups R bonded to Si atoms are oriented in a perpendicular direction to the inorganic layer,

alternatively pointing up and down the plane. The distance between two neighboring organic chains pointing in the same direction is 3.93 Å, which is close to the minimum distance at which alkyl chains can be packed [27,33]. The strong H-bonds among urea groups produced a strained Si–O–Si structure, a fact that was also evidenced by the location of the Si–O–Si antisymmetric stretching in the FTIR spectrum.

The proposed structure is similar to those reported for some silica surfaces. Hexagonal lattices of Si–O–Si bonds are present in the silica surface of tridymite and on the

(1 1 1) surface of β -cristobalite [33]. Bonds issuing from alternating Si atoms point up and down to the plane of the hexagon. Those pointing down are bonded to O atoms generating SiO_2 tetrahedra while those pointing up are bonded to OH groups (surface silanol groups) [33]. A similar structure is present in the inorganic layer of the silsesquioxane with the organic group R alternatively extending up and down from every Si atom.

4. Conclusions

By selecting an organotrialkoxysilane containing a urea group and a dodecyl chain in the organic moiety it was possible to produce the self-assembly of the resulting silsesquioxane into nanoparticles formed by an agglomeration of crystalline nanorods connected to an amorphous matrix. The self-assembly was produced by strong H-bonds among urea groups and tail-to-tail associations of organic groups. A colloidal solution of the silsesquioxane in methanol was used to produce coffee ring structures on the surface of carbon films. As a silsesquioxane with urea groups exhibits intrinsic photoluminescence, the described process leads to patterns of photoluminescent nanoparticles on the surface of carbon films. This opens the possibility of producing regular patterns by adapting the process to ink-jet printing techniques. Patterned optical surfaces might find applications in optoelectronics and light emitting devices.

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