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Design of hybrid nanomaterials based on silica-porphyrin. AFM characterization

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The present work describes some experimental studies regarding the obtaining and characterization of some new silica-porphyrin hybrid nanomaterials. A few experiments regarding porphyrin immobilization into silica matrix, based on tetraethoxysilane and tetramethoxysilane, by using different sol-gel techniques: *in situ*, by impregnation and by using sonication, are presented. The used *para*-hydroxyphenyl substituted porphyrin, namely: 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine, was isolated and purified by TLC, and column chromatography, after performing an Adler condensation reaction. The functional porphyrin was characterized by ^{1}H-NMR, MS, FT-IR and UV-vis spectrometry and the silica-porphyrin hybrid generations were monitored by AFM and UV-vis spectrometry. High-resolution imaging, using atomic force microscopy (AFM), has been applied to directly observe the surface structures which are formed by immobilization of porphyrins on the surfaces. AFM features show that nanocluster porphyrin stacks of various heights were formed on silica surfaces. It may be possible to affirm that the assembly of porphyrins was directed into a co-planar, stacked orientation. AFM images show that the porphyrin stacks do not merge more than two together. Cursor measurements indicate that the columnar stacks have variable heights, ranging from 2.4 to 18.5 nm.

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1. Introduction

Conventional solar cells using semiconducting materials such as silicon have contributed greatly to modern society. The use of photocurrent generating hybrid devices comprising organic molecules is now the state of art in this field [1].

In connection with previously applications of porphyrins [2] the potential advantages of this approach are to optimize light adsorption, surface binding, and charge transfer, with expected efficiencies in building of solar cells [3].

The majority of research on the photochemistry of porphyrins is an attempt to mimic the photosynthetic processes, in which porphyrins have been widely employed as sensitizers and as electron donors. Organic solar cells could benefit from diverse functions of modifiable organic compounds, not only regarding the efficiency for energy conversion, but also the light absorption wavelength (light color), form, and durability of devices can be controlled using synthetic approaches [4].

The present study is dealing with the obtaining of advanced transparent hybrid silica materials encapsulating 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine**, (TOHPP)**. They have been prepared successfully via the basic and the two steps acido-basic catalyzed hydrolysis and condensation of tetramethyl-orthosilicate **(TMOS)** and tetraethylorthosilicate **(TEOS)** using different approaches of the sol-gel process: : *in situ*, by impregnation and by using sonication. The synthetic conditions have been studied.

The obtained nanoporous materials usually exhibit high surface area, large pore volume and narrowly distributed pore diameter. Because of this novel sol-gel technology, under the temperatures at which organic compounds are thermally stable, the method was used to study behaviors of encapsulated macrocycles in silica matrix within a confined space.

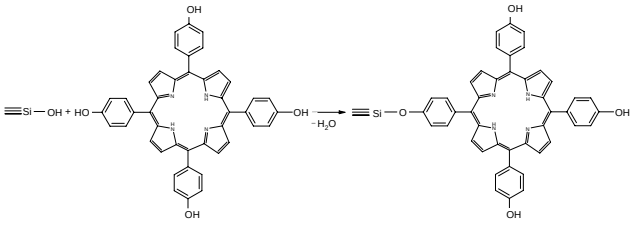
The sol-gel process involves two steps. Precursors initially form high molecular weight species but still soluble and mobile oligomeric intermediates, a sol. The intermediates further link together to form a three-dimensional crosslinked network, a gel. The precursors for a sol-gel reaction could either be inorganic or organic compounds [5]. Tetraethoxysilane and tetramethoxysilane, are the most widely used alkoxide precursors. In the first step, silicon alkoxides are hydrolyzed by mixing with water and either an acid or a base can serve as catalyst. The second step involves a lot of types of polycondensation reaction, as represented in the following equations (1-4):

$$\equiv Si—OR + H_2O \longrightarrow \equiv Si—OH + ROH$$

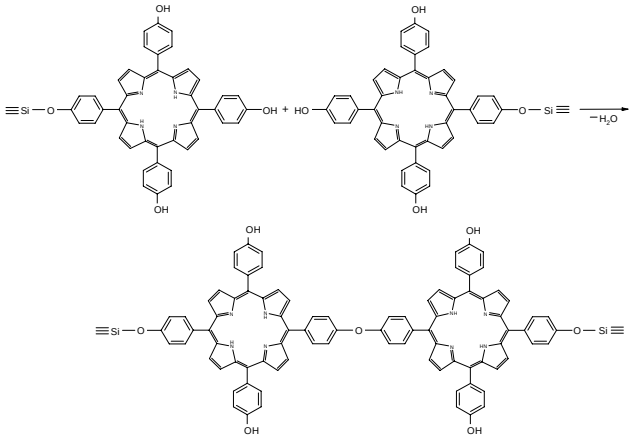
where R = CH_3, C_2H_5

$$\equiv Si—OH + \equiv Si—OR_1 \longrightarrow \equiv Si—O—Si\equiv + R_1OH \quad (2)$$

where R_1 = H, CH_3, C_2H_5



(3)



(4)

2. Experimental

Reagents: Tetramethyl orthosilicate (TMOS, 98%, Merck), Tetraethyl orthosilicate (TEOS, 98%, Fluka), tetrahydrofuran (THF, 98%, Merck), methanol absolute (MeOH, Chemopar) ethanol absolute (EtOH, Chemopar) were all used as received without further purification.

Apparatus: FT-IR (JASCO 430 FT-IR, KBr pellets) spectra were carried out, in the 4000-400 cm^{-1} range. UV-visible spectra were recorded on a UV/VIS PERKIN ELMER, LAMBDA 12 spectrometer. ^{1}H-NMR spectrum was registered on a 400 MHz Bruker spectrometer in $CDCl_3$ and chemical shifts are reported relative to internal TMS (0.0 ppm). The HPLC analysis were performed on a JASCO apparatus equipped with NUCLEOSIL C18 nonpolar column, and on KROMASIL SI 100 5um polar column, 240x4 mm with MD 1510 detector, at ambient temperature. A 212 Varian Finnigan Mat mass spectrometer was used for registering MS. Ultrasonic Cole Parmer Cleaning Bath, working at 56 KHz frequency; output power of 80W was used. Atomic force microscope (AFM) measurements were made with sample preparation onto a silica plate. Scanning probe microscopy investigations were carried out with an Atomic Force Microscope designed at Twente University of Holland. A Park Scientific microcantilever was used for performing measurements with a tip having a radius of curvature of around 20nm. The measurements are performed quantitatively on the plane of the measurement and in the direction perpendicular to the surface with lateral resolution of 20 nm and of 2 nm vertically, on maximum of 20x20 μ arias, the maximum admitted roughness of the samples being of 6 μ. Height image data obtained by the AFM is three-dimensional. The usual method for displaying the data is to use a colour mapping for height, for example black for low features and white for high features. All AFM measurements were done at ambient conditions (temperature: 21±2 °C; relative humidity: 50–70%).

Synthesis and purification of 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine, (TOHPP has been done according to modified literature methods, by adding stoechiometric amounts of propionic anhydride in order to increase the yield [6, 7].

***In situ* base catalyzed sol-gel method, starting from TMOS.** TOHPP (0.0073 g, 0.108 mmol) dissolved into 13.75 ml THF were put into a vessel and TMOS (2.89 g, 0.019 mol) dissolved into MeOH (0. 6045 g, 0.0189 mol) were added by slow dropping under vigorous stirring. After 15 minutes a solution consisting in 0.39 g NH_3 25% diluted with 1.0745 ml deionised water was added to the initial reaction mixture and the stirring was continued for an additional hour. The following molar ratios were kept constant during the synthesis: THF: MeOH = 9:1 and H_20: TMOS = 4:1. The final material was a transparent red stable gel. The wet gel was dried for two hours at 60°C, and the color turned to light green. The control sample was synthesized identically without porphyrin adding. A transparent gel was obtained.

***In situ* two steps acid/base catalyzed sol-gel method starting fromTEOS.** A mixture of H_2O (1.365 g, 0.076 mol) and HCl 37% (0.037 g, 1.01 mmol) were added by slow dropping under vigorous stirring to a solution of TEOS (3.95 g, 0.019 mol) dissolved into EtOH (3.49 g, 0.076 mol). The following molar ratios were kept constant during the first acidic step: TEOS: EtOH: H_2O: HCl =1: 4: 4: 0.02. After 15 minutes, the second basic step was started by slowly adding of NH_3 2.5%. At the moment of opalescence TOHPP (0.0073 g, 0.108 mmol) dissolved into 13.75 ml THF were added by once. The basic catalysis was controlled by slowly adding of a total amount of 1.09 g NH_3 2.5%. The final material was a transparent red stable gel. After the wet gel was dried for 8 hours at 100°C, the color turned into green. The control sample was identically synthesized, without porphyrin adding, and by using a total amount of 1.62 g solution of NH_3 2.5%. A transparent gel was obtained.

Porphyrin entrapping by impregnation within a silica matrix derived from a two steps acid/base sol-gel process, by using TEOS as precursor. A mixture of H_2O(1.365 g, 0.076 mol) and HCl 37% (0.037 g, 1.01 mmol) were added by slow dropping under vigorous stirring to a solution of TEOS (3.95 g, 0.019 mol) dissolved into EtOH (3.49 g, 0.076 mol). The following molar ratios were kept constant during the first acidic step: TEOS: EtOH: H_2O: HCl =1: 4: 4: 0.02. After 15 minutes, the second basic step was started by slowly adding of 0.71 g NH_3 2.5% until a transparent gel was obtained. TOHPP (0.0073 g, 0.108 mmol) dissolved into 13.75 ml THF were added by once to the gel, which exhibit after shaken and stirring the property of tixotropy. The stirring of the fluidized gel is continued and after 15 minutes the gelation is finished, resulting a red transparent gel. The control sample was synthesized identically without porphyrin

adding and by using a total amount of 0.93 g NH_3 2.5%. A transparent gel was obtained.

***In situ* sol-gel method using TEOS by sonication** was conducted in acido-basic catalysis by porphyrin impregnation, in identical previously described conditions. Amounts of 0.4 and 0.57 g NH_3 2.5% for the porphyrin-sol-gel compound, respectively for the control sample were necessary. During the sonication (110 minutes), the temperature increased from 25 °C to 48°C. The porphyrin-sol-gel hybrid material was jellified after 24 hours, resulting in a red transparent gel. An observation is to be done: during last minutes of mixing, the organic phase and inorganic phase were separated, so the reaction mixture looked translucent, and suddenly after the solution turned into transparent gel.

3. Results and discussion

The main spectrometric characteristics of free base porphyrin are given bellow:

5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine, dark violet-reddish crystals, η= 19%, FT-IR(KBr), cm^{-1}: 747 (γ C-H $_{Ph}$), 802(γ C-H $_{Pyrrol}$), 967(ν C-N), 1172 (δ C-H $_{Pyrrol}$), 1466 (ν C=N), 1492 (ν C=C $_{Pyrrol}$), 1512 (ν C=C $_{Ph}$), 1601 (ν C=C $_{Pyrrol}$), 3317 (ν N-H), 3415 (ν O-H). ^{1}H-NMR ($CDCl_3$, 400MHz),δ, ppm: -2.81 (s, 2H, NH), 7.36- 7.38 (d, 8H, 3,5 H- Ph (*meso*)), 8.06- 8.11 (d, 8H, 2,6 H- Ph (*ortho*)), 8,98(s, 8H, β-H), 10.01(s, 4H, OH). UV-Vis ($CHCl_3$) - λ max(log ε): 419.68(5.01); 450.63(4.17); 515.97(3.98); 551.48(3.78); 590.56(3.63); 649.32(3.56). UV-Vis (hexane) -λmax (logε): 417.55(4.81); 516.27(3.99); 552.37(3.79); 590.48(3.64); 648.55(3.53). MS-m/z (relatively abundance): 678 ($M^{+\cdot}$ = $C_{44}H_{30}N_4O_4]^{+\cdot}$), 356 (14.75%), 307 (22.27%), 293 (24.99%), 121 (77.33%), 94 (55.18%), 77 (10.70%), 56 (100%).

The sol-gel processes, by using TMOS and TEOS as silica polymeric backbone sources have been monitored by UV-vis spectroscopy.

As expected, the spectrum of the silica control sample without porphyrin possessed no absorption bands in the UV-vis range.

A comparison of the UV-vis spectrum of porphyrin free-base with that of the hybrid silica –porphyrin material obtained at the gelation point (Fig. 1) put into evidence two major differences.

The *etio* type spectrum of the porphyrin in tetrahydrofuran, presents the Soret band at 418.96 nm arising from transition of a_{1u} (π) - e_g^* (π), and the other four absorption Q bands around 514.99, 550.38, 593.20 and 650.55 nm corresponding to a_{2u} (π) - e_g^* (π) transitions.

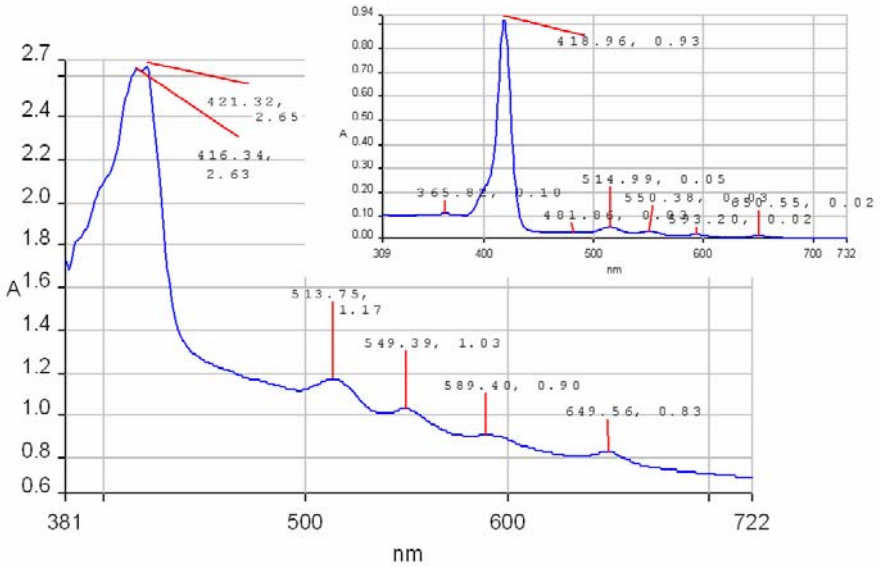


Fig. 1. UV-vis Spectrum of sol-gel sample at the gelation point and UV-vis spectrum of the porphyrin free-base (small-size), in tetrahydrofuran Hybrid material - λ max (log ε): 421.32 (5.03); 416.34(5.03); 513.75(4.68); 549.39(4.62); 589.40(4.56); 649.56(4.53). Porphyrin free-base λ max (log ε): 418.96 (4.92); 514.99(3.65); 550.38(3.43); 593.20(3.25); 650.55(3.25).

UV-vis Spectrum of sol-gel sample at the gelation point is similar to the spectrum of free base TOHPP excepting that all the absorption bands, especially Q bands, exhibit a hiperchromic effect when TOHPP is encapsulated in silica matrix (Fig. 1). A photoactivity increase of at least 128% is to be underlined in the range of all four Q bands (500-650 nm) of porphyrin-silica matrix sample (log ε>4.5) in comparison with the Q bands of the free-base porphyrin (log ε<3.65).

The second difference is that concerning with the splitting of the Soret band with a band batochromic shifted and a band hypsochromic shifted which is significant for this process, according to side-reaction (Equation 4), providing that the dye molecules tend to aggregate by *π–π* and hydrophobic interactions [8].

High-resolution imaging using atomic force microscope (AFM) has been applied to directly observe the surface structures which are formed by immobilization of porphyrins on the surfaces. The force between the tip

and the sample surface is detected and kept constant throughout the scan and hence yields the topography of the surface. Three dimensional AFM images (Fig. 2, 3) and two dimensional profiles (Fig. 4-8) available from cross-sectioned samples were obtained. The dry samples were investigated by AFM in the contact mode in a range of scan lengths from 15 to 1μ.

AFM features show that nanocluster porphyrin stacks (Fig. 2,3) of various heights were formed on silica surfaces. It may be possible to affirm that the assembly of porphyrins was directed into a co-planar, stacked orientation.

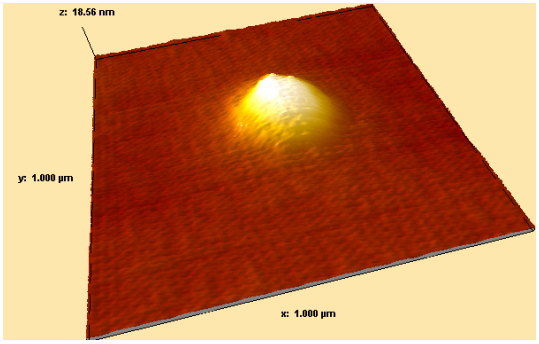


Fig. 2. 3D AFM Image (1 x 1 μm) of hybrid material obtained by In situ base catalyzed sol - gel method, starting from TMOS.

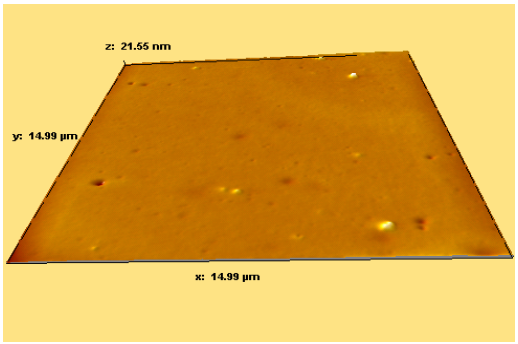


Fig. 3. 3D AFM Image (15 x 15 μm) of hybrid material obtained by In situ base catalyzed sol - gel method, starting from TMOS.

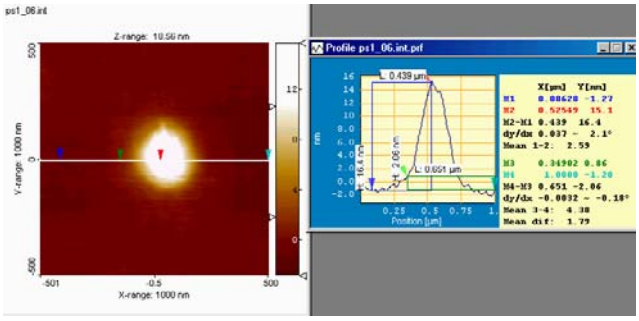


Fig. 4. 2D AFM Image-profile (1 x 1 μm) of hybrid material obtained by In situ base catalyzed sol - gel method, starting from TMOS.

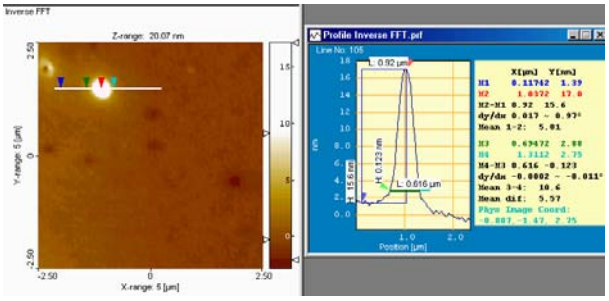


Fig. 5. 2D AFM Image-profile (5 x 5 μm) of hybrid material obtained by In situ base catalyzed sol - gel method, starting from TMOS.

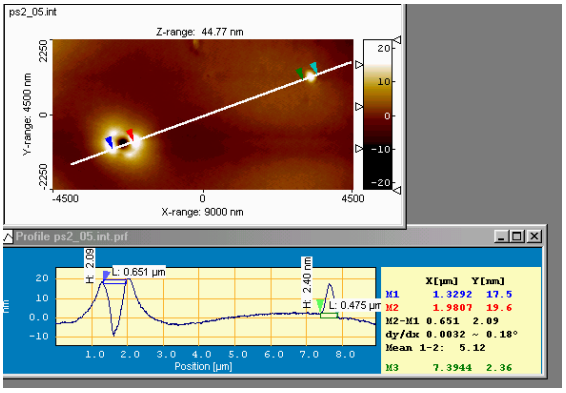


Fig. 6. 2D AFM Image-profile (9000 x 4500 nm), of the hybrid material obtained by impregnation of porphyrin within a silica matrix derived from a two steps acid/base sol-gel process, by using TEOS as precursor.

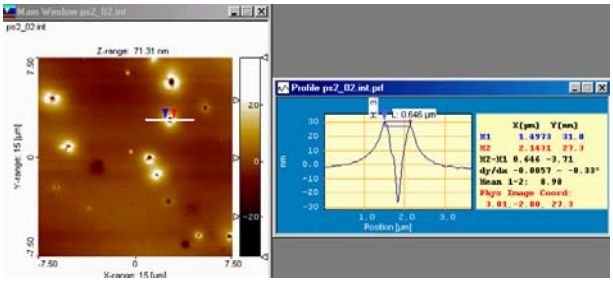


Fig. 7. 2D AFM Image-profile (15 x 15 μm) of the hybrid material obtained by impregnation of porphyrin within a silica matrix derived from a two steps acid/base sol-gel process, by using TEOS as precursor.

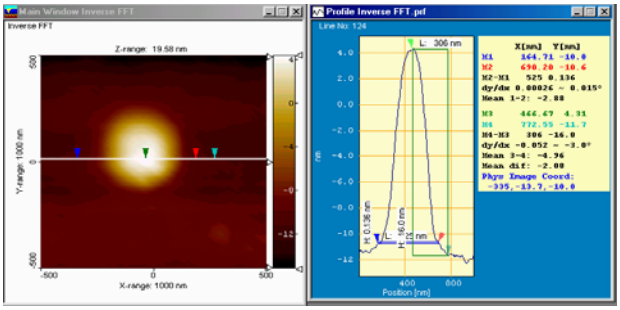


Fig. 8. 2D AFM Image-profile (1 x 1 μm) of hybrid material obtained by In situ two steps acid / base catalyzed sol-gel method starting from TEOS.

Cursor measurements (Fig. 4-8) indicate that the columnar stacks have variable heights, ranging from 2.4 to 18.5 nm, up to maximal value of 31 nm. AFM studies of porphyrin-silica hybrid materials have shown that these structures are varying between 300-650 nm in width.

The most of the porphyrin aggregates consisting of oblong nanoparticles are 16-18 nm in height. This is in agreement with the literature [9] specifying that small substituents on the 4-position of tetraaryl porphyrins favour π stacking, whereas those on 2 or 3 position prevent significant π stacking.

AFM images (Fig. 6,7) show that the porphyrin stacks do not merge more than two together and that are separated by distances of at least 700nm. This tendency to aggregation was also revealed by UV-vis spectroscopy and is in connection with the splitting of the Soret band of the hybrid silica-porphyrin nanomaterial (Fig. 1).

The oval shape stacks are aligned after parallel direction rather than having a random orientation, as shown in Fig. 7.

Analyzing the AFM images, it can be concluded that the merging process of porphyrin stacks is occurring only when methods implying an acidic step were used. In case of *in situ* base catalyzed sol-gel method, starting from TMOS, the porphyrins stacks do not merge together, being solitary (Fig. 2).

4. Conclusions

The present study is concerned about new inorganic-organic hybrid materials consisting in 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine encapsulated in silica matrix. Preliminary tests meant to optimize immobilization process in one-step basic and two steps acid-base catalysis, by using different sol-gel techniques: *in situ*, by impregnation and by using sonication are presented.

Porphyrin molecules are introduced into silica gels without major changes regarding their photoactivity, but with a side reaction of porphyrin aggregation, and hiperchromic effects regarding Q bands.

High-resolution imaging using atomic force microscopy (AFM) has been applied to directly observe the surface structures which are formed by immobilization of porphyrins on the surfaces. AFM features show that nanocluster porphyrin stacks of various heights were formed on silica surfaces. It may be possible to affirm that the assembly of porphyrins was directed into a co-planar, stacked orientation. AFM image show that the porphyrin stacks do not merge more than two together, underlying the UV-vis experimental remarks concerning about porphyrin aggregation.

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