

**BASE CATALYZED SOL-GEL METHOD STARTING FROM TMOS FOR
SYNTHESIS OF SILICA-PORPHYRIN NANOMATERIAL. FT-IR AND AFM
CHARACTERIZATIONS**

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Abstract

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. An experiment regarding porphyrin immobilization into silica matrix by using *in situ* sol-gel technique starting from TMOS is 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 and the silica-porphyrin hybrid material were monitored and characterized by ¹H-NMR, FT-IR and UV-vis spectrometry. High-resolution imaging using atomic force microscopy (AFM) have been applied to directly observe the surface structures which are formed by immobilization of porphyrin on the surfaces.

Keywords: porphyrin, hybrid material, sol-gel method.

1.Introduction

Applications of sol–gel derived biomaterials include selective coatings for optical and electrochemical biosensors [1], stationary phases for affinity chromatography, immunoadsorbent and solid-phase extraction media [2], solid-phase biocatalysts [3].

The present study is concerned about obtaining of transparent hybrid silica materials encapsulating 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine, (TOHPP). They have been prepared successfully via the basic catalyzed hydrolysis and condensation of tetramethylorthosilicate (TMOS) using *in situ* sol-gel process.

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. Tetramethoxysilane (TMOS), was used as alkoxide precursor. The compositions were characterized by using spectroscopic and microscopic methods such as FT-IR and AFM.

2. Method and samples

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. $^1\text{H-NMR}$ spectrum was registered on a 400 MHz Bruker spectrometer in CDCl_3 . A 212 Varian Finnigan Mat mass spectrometer was used for registering MS. Atomic force microscope (AFM) measurements were made with deposition of the hybrid material on silica plates.

Reagents: Tetramethyl orthosilicate (98%, Merck), pyrrole (98%, Fluka), propionic acid (98%, Fluka), *p*-hydroxi-benzaldehyde (98%, Fluka), tetrahydrofuran(THF, 98%, Merck), methanol absolute (MeOH, Chemopar) ethanol absolute (EtOH, Chemopar) were all used as received, except for pyrrole which was distilled prior to use.

Synthesis of 5,10,15,20-tetrakis(4-hydroxyphenyl)-21H,23H-porphine, (TOHPP) has been done according to modified literature methods in order to increase the yield [4].

***In situ* base catalysed sol-gel method using TMOS:** TOHPP (0.0073g, 0.108mmol) 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, 0.0189mol) were added by slow dropping under vigorous stirring. After 15 minutes a solution consisting in 0.39g 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_2O : TMOS = 4:1. The final material was a transparent red stable gel. The wet gel was dried for two hours at 60°C. The control sample was synthesized identically without porphyrin adding. A transparent gel was obtained.

3. Results and Discussions

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

5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine, dark violet-redish crystals, $\eta = 19\%$, FT- IR(KBr), cm^{-1} : 747 (γ C-H_{Ph}), 802(γ C-H_{Pyrrol}), 967(v C-N), 1172 (δ C-H_{Pyrrol}), 1466 (v C=N), 1492 (v C=C_{Pyrrol}), 1512 (v C=C_{Ph}), 1601 (v C=C_{Pyrrol}), 3317 (v N-H), 3415 (v O-H). $^1\text{H-NMR}$ (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). MS-m/z (relatively abundance): 678 ($\text{M}^+ = \text{C}_{44}\text{H}_{30}\text{N}_4\text{O}_4]^+$), 356 (14.75%), 307 (22.27%), 293 (24.99%), 121 (77.33%), 94 (55.18%), 77 (10.70%), 56 (100%).

The chemical structure of hybrid materials, of TOHPP and control samples are characterized with a FT-IR spectroscopy as shown in Figure 1.

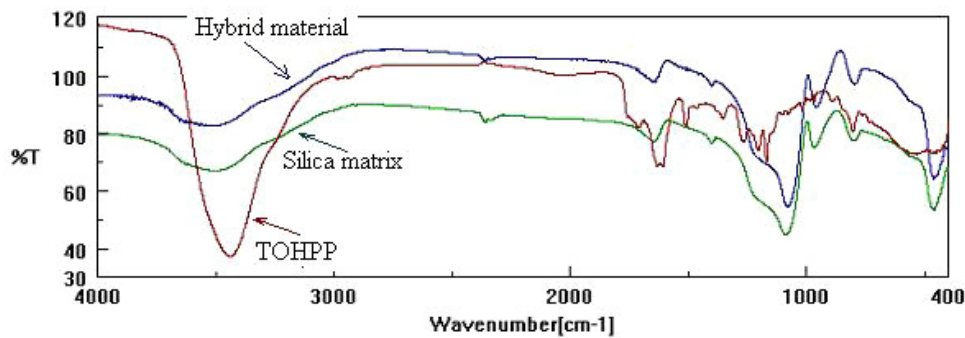


Figure 1. FT-IR of superposed TOHPP, hybrid material and control silica matrix sample.

In situ base catalyzed sol-gel method, starting from TMOS

Both spectra of silica-control sample and porphyrin-silica material exhibit a broad band between 3100 and 3700 cm^{-1} related to the presence of Si-OH, and to the inter- and intramolecular hydrogen bonds. The difference between these two spectra can be noticed within the 1300 - 1000 cm^{-1} region. The bonding mode from 1090 to 1150 cm^{-1} is assigned to the Si-O-Si asymmetric stretching mode. The bonding modes near 1065 cm^{-1} and 1105 cm^{-1} can be assigned to the Si-O-C asymmetric stretching. In the spectrum of hybrid material registered in this region, the bands of TOHPP bending-groups were not clearly identifiable because they overlap with the broad bands of Si-O-Si and Si-O-C in hybrid material [5]. This feature [6] could indicate that silica inorganic component was covalently bonded to the organic component TOHPP. The presence of the identified Si-O-Si and Si-O-C bonds demonstrates that the hybrid materials contain inorganic network. The Si-O-C may result from the interaction between the Si-O network and the hydroxy-porphyrin.

High-resolution imaging using atomic force microscopy (AFM) have been applied to directly observe the surface structures (Figures 2-3) which are formed by immobilization of porphyrin on the surfaces.

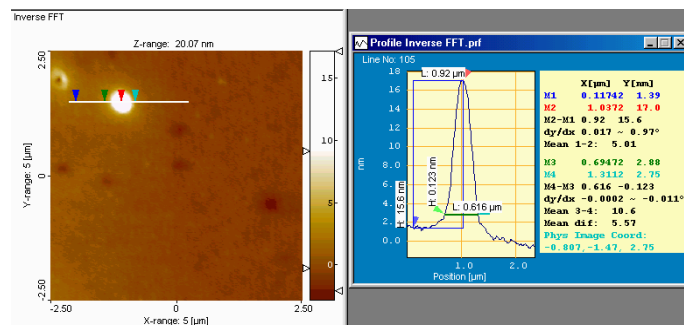
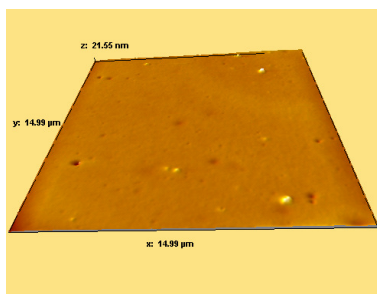


Figure 2. 3D AFM Image (15 x 15 μm) Figure 3. 2D AFM Image-profile (5 x 5 μm)

The assembly of porphyrins was directed into a co-planar, stacked orientation. AFM images show that the porphyrin stacks do not merge together and are separated by distances of at least 700nm. 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 [7] specifying that small substituents on the 4-position of tetraaryl porphyrins favor π stacking, whereas those on 2 or 3 position prevent significant π stacking.

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, starting from TMOS. The obtained hybrid materials correspond to compounds, Class II, where organic and inorganic components are linked through strong covalent chemical bonds [8]. If the the organic/inorganic component ratio was taken into consideration [9], the obtained hybrid materials represent *organics doped systems* (porphyrine, less than 1%).

Acknowledgements

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