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Article

HYBRID SILICA-PORPHYRIN NANOMATERIALS SENSITIVE TO GAS DETECTION

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Abstract

Meso-tetratolylporphyrin encapsulated in a silica matrix leads to a porous hybrid nanomaterial that was tested to CO_2 detection. For experimental purposes, the material was solved in THF and a continuous flow of CO_2 gas was introduced to the solution. The response of the material to gas adding was measured using UV-Vis spectra and colorimetric changes. The dependence of the absorption intensity of the Soret band and the CO_2 concentration is linear with a fair correlation coefficient of 0.92 but the establishment of equilibrium for the reversible CO_2 indicator has to be improved.

Keywords: *meso*-tetratolylporphyrin, hybrid silica materials, UV-Vis, AFM, CO_2 detection

1. INTRODUCTION

Due to the well-known amazing photosensitive properties of natural and synthetic porphyrins and because of their high reactivity, researchers have tried to enhance these exceptional qualities by combining different porphyrins with various metal colloids, polymers or silica precursors to obtain various nanomaterials [1,2].

The demand for safe environmental conditions led to the development in gas sensor approaches and technology. Metal-organic frameworks (MOFs) combined with porphyrin nanoassemblies have great potential in gas storage, gas separations, catalysis, and sensing [3].

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Thus, immobilized complexes of Pd-porphyrin in clay minerals are exceptionally suitable and economically affordable to be used as efficient optical oxygen sensors [4].

A sensitive structure consisting of 5,10,15,20-tetrakis(3,4dimethoxy-phenyl)-porphyrin Fe(III) chloride and single walls carbon nanotubes (SWCN) included in a Ba stearate matrix was used for the development of a sensor by depositing the nanomaterial on a ceramic substrate with platinum interdigital electrodes. The sensor proved a strong sensibility to UV irradiation [5]. Tests performed upon this material also showed that the manufactured sensor presents good sensitivity toward O_2 ionization [6].

Other inorganic scaffolds used for this purpose were: SWCN in combination with iron(III) protoporphyrin IX, applied on a graphite electrode that was used as reduction agent for H_2O_2 [7].

Hybrid materials obtained from the encapsulation of 5,10,15,20-tetratolyl-21H,23H-porphyrin in silica matrices have been previously prepared [8] and their morphological properties were characterized. Beside the content of porphyrin dye, the use of this kind of mesoporous material as potential gas detector (CO_2 in this case) is justified by the high surface area and large pore volume. The material was obtained by in situ two steps acid–base catalyzed sol–gel method, starting from TEOS.

The present study is based on pH dye-based indicators, in which the gas carbon dioxide dissolves in aqueous solution to form carbonic acid; the acid can dissociate to generate protons, which react with the porphyrin indicator producing a color change due to the obtainment of mono- and di-protonated porphyrin species.

2. EXPERIMENTAL METHOD

Apparatus

The spectrometer used for recording UV spectra was a UV-vis JASCO V-650 apparatus. Cuvettes were 1 cm quarz glass. Measurements were done in the range of interest 350-750 nm.

Atomic force microscopic surface imaging was performed on Nanosurf[l] EasyScan 2 Advanced Research apparatus from samples deposited on silica plates. Measurement conditions were environmental, using contact or tapping mode. The investigated scan areas were maximum 9 µm x9 µm, with lateral resolution of 20 nm and vertical resolution of 2 nm.

QUANTACHROME Nova 1200 apparatus was used for the determination of pore size, by using nitrogen as adsorbate, at the temperature of liquid nitrogen 77.350K. The method for calculation was de Boer's (programme Quantachrome NovaWin2 - Data Acquisition and Reduction for NOVA instruments ©1994-2003, Quantachrome Instruments, version 2.1). Thermogravimetric analysis was performed with a Paulik & Erdey D type derivatograph. The measurements were conducted in air using a platinum crucible. The heating rates were 5K/min.

Hybrid synthesis

The hybrid material was obtained and has been fully characterized as previously reported [8] and the silica glass obtained by in two steps acid-base catalysis was used for the experiments, due to its corresponding pH characteristics.

Testing of CO_2 sensitivity

Porphyrin –silica hybrid material (1 g) solved in 30 mL THF and 5 mL H_2O was sealed in a 50 mL Erlenmeyer flask equipped with a magnetic stirrer. Through the cork a syringe needle was introduced to the bottom of the flask and CO_2 gas was bubbled (1mL/min) under intense stirring. The cork was envisioned with a supplementary needle through which the samples were extracted, without affecting the gas flow through the solution and the equilibrium reactions. Samples were extracted every 15 minutes or by exact time monitoring and were characterized by UV-vis spectra (Figure 3).

3. RESULTS AND DISCUSSIONS

Amorphous inorganic solids that contain immobilized porphyrins can be obtained by sol–gel processes at environmental temperatures. These hybrids usually retain the optical properties of the encapsulated organic compound. The structure and properties of the nanomaterials can be easily designed by controlling the preparation conditions.

In case of silica, using one step acid catalysis transparent gels of low porosity are obtained, whereas with basic catalysts gels of higher porosity are made [9].

Using tetraethyl-orthosilicate (TEOS) as precursor, silica gels were obtained by hydrolysis and condensation reactions in EtOH/water solutions at room temperature. For the first hydrolysis step hydrochloric acid was used as catalyst. In the second condensation step ammonia was used as catalyst. It is well-known that the molar ratio between water and tetraethylorthosilicate as well as the pH of the gelation point significantly influences the properties of the obtained material [8].

Hybrid materials obtained from the encapsulation of 5,10,15,20-tetratolyl-21H,23H-porphyrin (Figure 1) in TEOS-based silica matrices were tested for potential CO_2 gas detection. The calculation by de Boer method for the hybrid material used in the experiments reveals the cumulative pore volume of 0.14 cm^3/g and a large surface a surface area of 326.6 m^2/g. The pore size are in the range of 1.377-2.60 nm.

The UV-vis spectrum of the bare 5,10,15,20-tetratolyl-21H,23H-porphyrin in THF is *etio*-type. The Soret band, of the highest energy, is located at 417 nm and has been assigned to the $S_0 \rightarrow S_2$ transition while the four lower energy bands, namely Q-bands, have been assigned to the $S_0 \rightarrow S_1$ transition [8]. The spectrum of the hybrid material solved in the same solvent presents the same shape but the lower intensities of the Q bands because of the interactions of the porphyrin molecules with the silica matrix (Figure 3).

By increasing the CO2 concentration in the solution, the registered spectra of the hybrid samples show a constant increase of the Soret band intensity. The decrease in the number of Q bands is attributed to the increase of the acidity in the tested porphyrin-silica solution.

As can be seen in Figure 4, the dependence of the absorption intensity of the Soret band and the CO_2 increased volume is linear. The correlation coefficient of 0.919 represents a promising response of the material to the presence of the gas. We have to mention that the reversibility time takes too long and will be further improved.

Figure 1: The structure of the 5,10,15,20-tetratolyl-21H,23H-porphyrin used to obtain the hybrid silica material

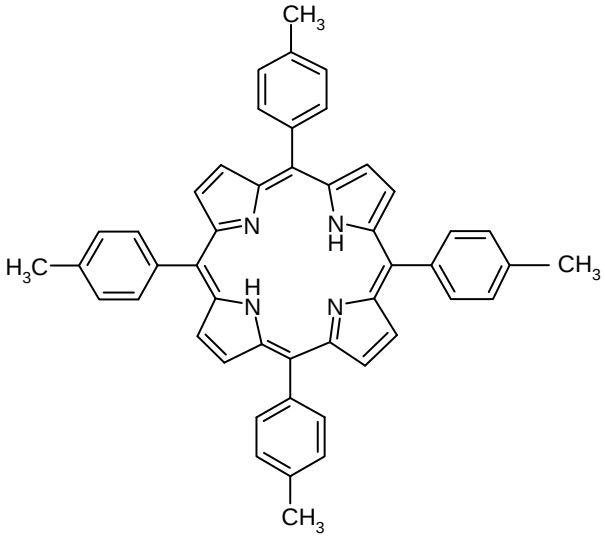


Figure 2: The UV-vis spectrum of the hybrid material solved in THF

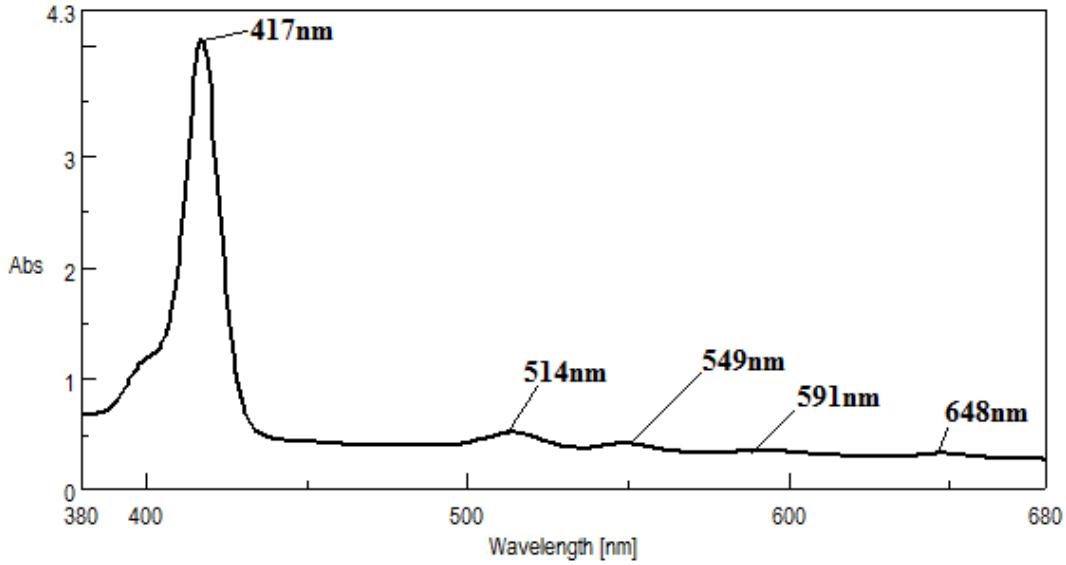


Figure 3: The superposed UV-vis spectra of the THF-water solution of the hybrid material at increasing CO_2 concentration

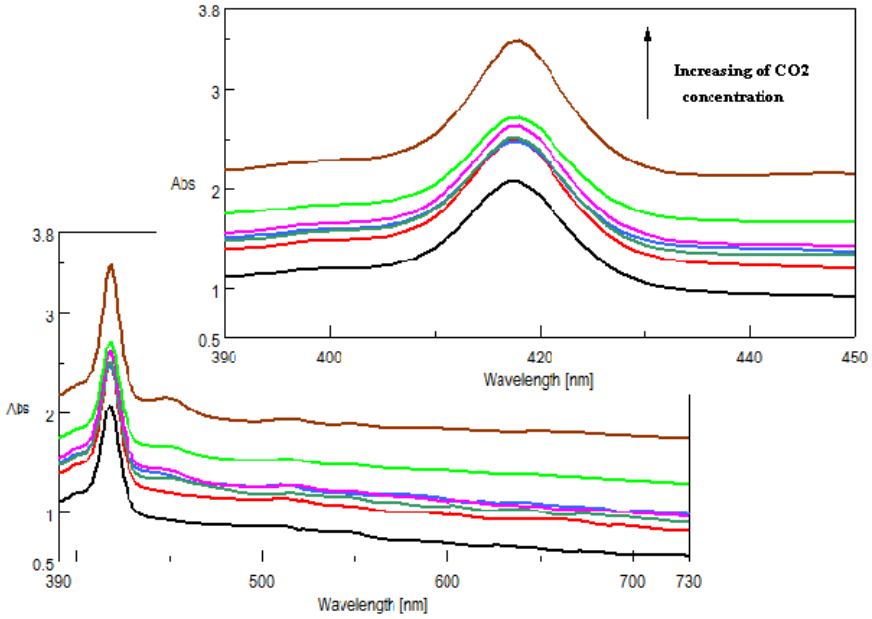
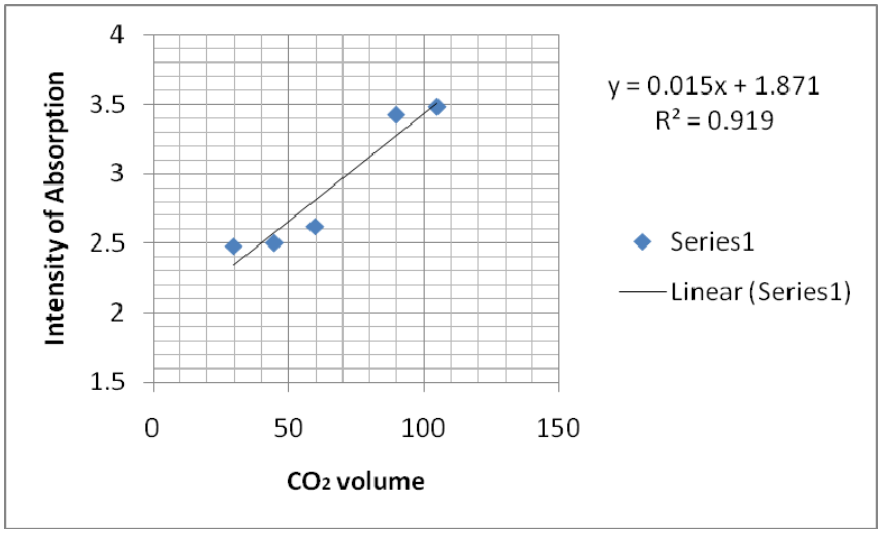
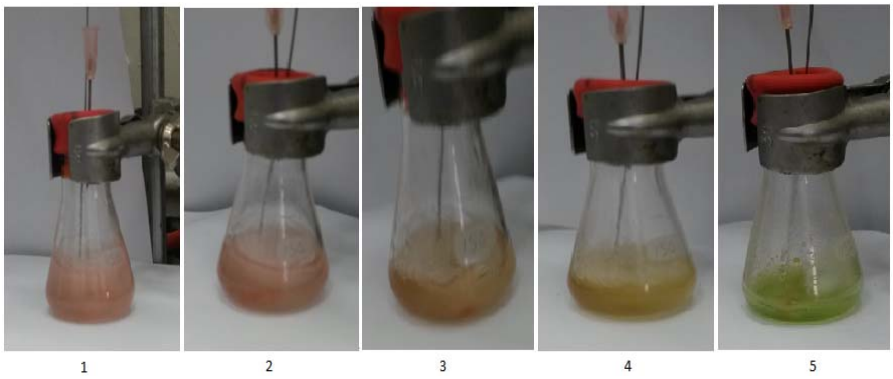


Figure 4: The correlation coefficient between the absorption intensity and the CO_2 gas volume



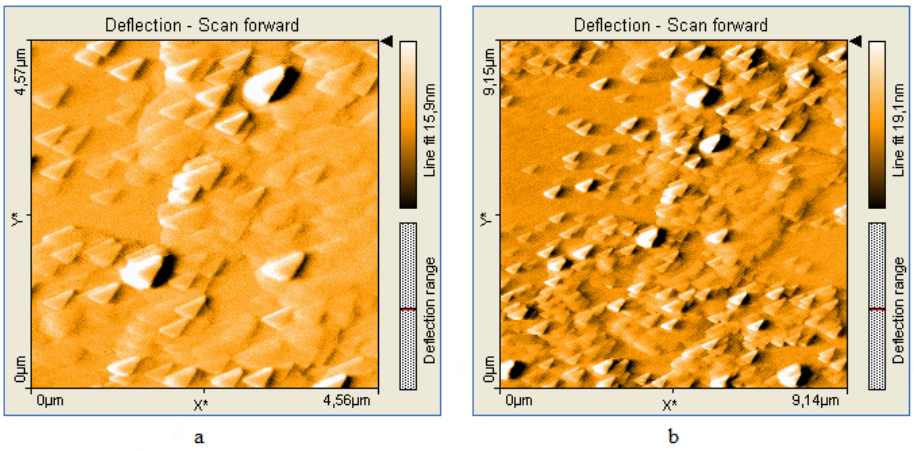
The color of porphyrins suffer changes during the experiments as response to different pH media and this is also a useful tool in detecting of carbonic acid in the solution. This change of color was evidenced by taking snapshots of the solution at the various stages of gas introduction (Figure 5).

Figure 5: The color changes during the gassing process **1**: the hybrid material before the introduction of CO_2 gas; **2-5**: the hybrid material at various stages of constant CO_2 flow



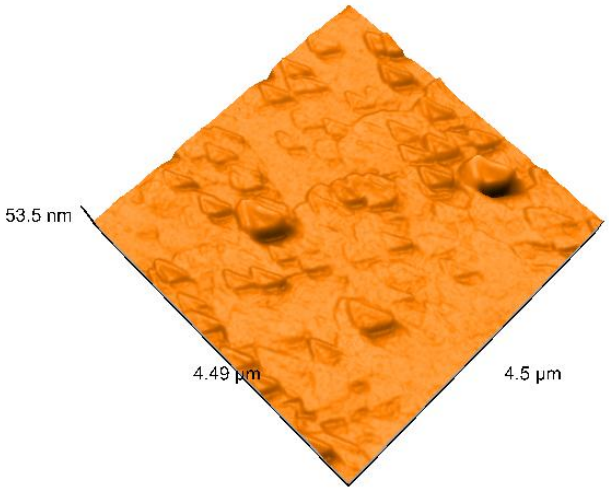
The AFM images performed on the hybrid material solved in THF and deposited by drop casting on silica plates are presented in Figure 6 a and b. It can be observed that the porphyrin molecules have a tendency to aggregate in triangular platelets, consistent with their already reported behaviour [8]. These aggregates are evenly oriented and of the same sizes.

Figure 6: 2D AFM images of the hybrid material solved in THF and deposited by drop casting



The 3D AFM image presented in Figure 7 outlines the formation of superposed triangular structures, corresponding to sandwich H-type aggregates, with dimensions ranging in the 370-480 nm domain.

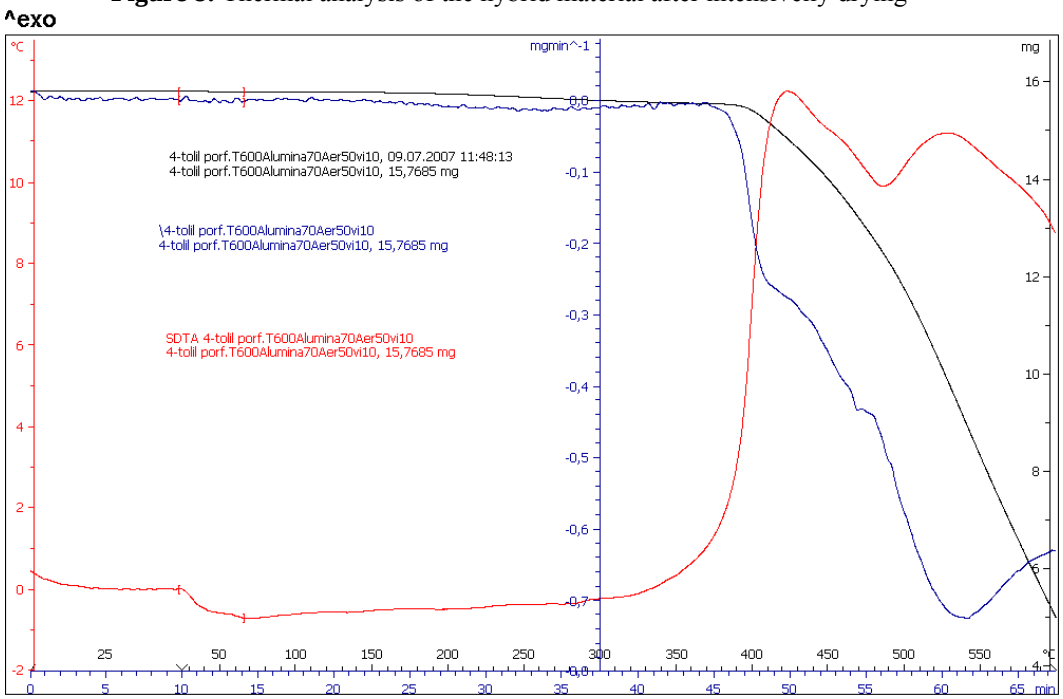
Figure 7: 3D AFM image of the hybrid material



Particle analysis offer information about the mean surface of islands, that is 0.0206 μm^2. The particles have a mean height of 0.8 nm, but the highest peak is arround 40 nm. The mean rugosity is of 3.9 nm.

According to thermal analysis the hybrid is stable to thermal treatment at least up to 350 °C (Figure 8). High thermal stability is the main requirement in porous materials that can be used in the fabrication of potential gas sensor devices.

Figure 8: Thermal analysis of the hybrid material after intensivelly drying



4. CONCLUSIONS

Hybrid silica-porphyrin materials, obtained from TEOS by in situ two steps acid–base catalyzed sol–gel method, show a great potential toward the sensing of gases due to large pore volume and surface area of the microporous material and also because its high thermal stability. The optical properties of such materials essentially maintain those of the organic dye chosen to be incorporated in the anorganic matrix. The 5,10,15,20-tetratolyl-21H,23H-porphyrin –silica hybrid is suited for optical/colorimetric formulation for CO_2 sensors if the time for reversible process will be improved. The dependence of the absorption intensity of the Soret band and the CO_2 concentration is linear with a fair correlation coefficient of 0.92.

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