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Spectroscopic and SEM Investigation of TCPP in Titanium Matrix

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Abstract**—**Titanium gels doped with water-soluble cationic porphyrin were synthesized by the sol–gel polymerization of Ti $(OC_4H_9)_4$. In this work we investigate the spectroscopic properties along with SEM images of tetra carboxyl phenyl porphyrin when incorporated into porous matrix produced by the sol–gel technique.

Keywords**—**TCPP; Titanium matrix; UV/Vis spectroscopy; SEM.

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I. Introduction

MICROPOROUS Porphyrin and Metalloporphyrin Materials are investigated by Margaret E. Kosal and Kenneth S. Suslick[1] The exploration of metalloporphyrin assemblies as building blocks for tailored materials properties has found rapid growth during the past decade[2]. Sol-gel-based optical sensors for both gas-phase and dissolved oxygen have been developed [3]. Both sensors operate on the principle of fluorescence quenching of a ruthenium complex which has been entrapped in a porous sol-gel silica film [4]. New materials porphyrinosilica and metalloporphyrinosilica template have been obtained by a sol-gel processing [5].Where functionalyzed porphyrins and metalloporphyrins "building blocks" were assembled into a three-dimensional silicate network. The catalytic activities of this metalloporphyrinosilica- template were compared [6].

It was observed before that the epoxidation of (Z)-cyclooctene was ten times faster in FeP homogeneous system than in the modified silica supported system (Lindsay Smith 1994) [7]. The major driving forces operating in these architectures are considered to be Π-Π stacking and/or van der Waals interactions. It is possible to fabricate these one-dimensional aggregates by inorganic materials, utilizing electrostatic and/or hydrogen-bonding interactions, to produce novel fibrous organic-inorganic hybrid materials [4, 8-11]. Many of them, such as chlorophylls [12], haemoglobin [13], and cytochromes [14], are essential in bio catalytic reactions. Inorganic–organic hybrids are now attracting much attention in terms of new useful materials. Silica gel [15], zeolite [16], titanium [17], have been used as inorganic supports due to their rigidity, stability, and capacity to absorb ions and molecules. The molecular imprinting technique is proven to be useful for the synthesis of heterogeneous catalyst with controlled architectures via templating routes [18]. The photophysics of dye-matrix systems, with both silica and titanium matrixs produced by sol-gel techniques have been studied. In here we studied the incorporation of TCPP in titanium matrix, as it is shown in Fig.1.

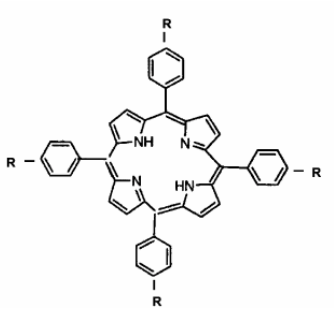


Fig.1 R=COOH,5,10,15,20-tetrakis (4-carboxylphenyl) porphyrin, TCPP

In this work we report the steady-state and time resolved photoluminescence of tetra (carboxylphenyl) porphyrine when incorporated in TiO_2 matrixes produced by sol-gel process. Morphological and structural characterization of matrix was also performed, it has been observed that reversible protonation and J-aggregate of porphyrin occurs on incorporation into sol-gel derived matrix.

II. Experimental Section:

(a) By following the Adler's method,the compound 5, 10, 15, 20-tetrakis (4-carboxylphenyl) porphyrin was synthesized by mixing the reagents 4-carboxy benzaldehyde, pyrrole and propionic acid,then the mixuture was refluxed for 2 hour. (b) The titanium matrix synthesized by mole ratio of [Ti $(OC_4H_9)_4$]: [Ethanol]: [H_2O deionized] 1:25:1 and HCl, for catalyst, dispersions was further stirred for 3 h, and subsequently, we can dope porphyrins in titanium matrix by solving them in ethanol. The absorbance and transmittance spectra were measured on a shimadzu UV-visible spectrophotometer along with the FT-IR spectrum of porphyrin and sol gel.

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III. RESULTS AND DISCUSSION

A. IR spectrum

At the IR spectrum, the peak at 3300 cm^{-1} is for N-H, 3400 is for O-H of carboxyl acid in TCPP. The peaks at 1700-1725 cm^{-1} are also related to carboxyl acid of TCPP, indicating that these molecules are aromatic. The solution of TCPP exhibits five absorption maxima; the sharp single Soret band at 414 nm and four maxima in the ''Q'' range 500-650 nm at 517, 554, 579 and 634 nm. The theoretically simple designed structure of Titanium gel is shown in Fig.3. The FT-IR spectrum (KBr) showed the peaks at1097 and 1125 cm^{-1} which can be assignable to the Ti-OEt groups are disappeared, while the newly appearance of broad peak at 1130 cm^{-1} is assignable to the Ti-O-Ti group, indicating that sol-gel polycondensation proceeds successfully, and the peaks at 1125 cm^{-1} and 1097 cm^{-1} changed before and after the reaction, this result suggests that the hydrogen-bonding network is scarcely damaged by the reaction.

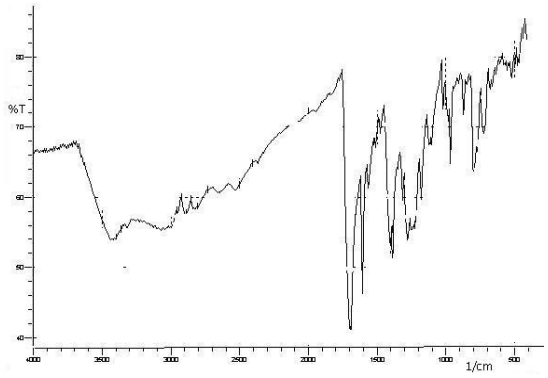


Fig. 2 IR spectrum of TCPP

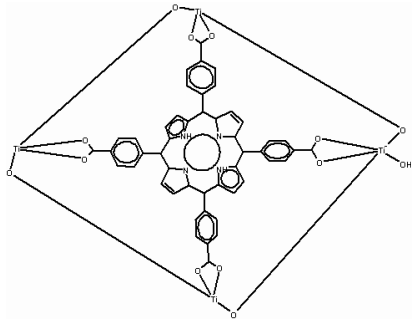


Fig. 3 Structure of Titanium gel doped with TCPP

B. UV-VisAbsorption

The intensity of the Soret band of porphyrin in sol–gel material is insignificantly lower than in water solution, the Soret bands in sol–gel besides broadening, it is also red shifted, in addition, the molar extinction coefficient is lower in sol-gel than in water. In the gel phase soret bond of H_2TCPP shifted to longer wavelength 420.0 nm, indicating that it assembles into a J-aggregate in the gel phase, Figure 5.

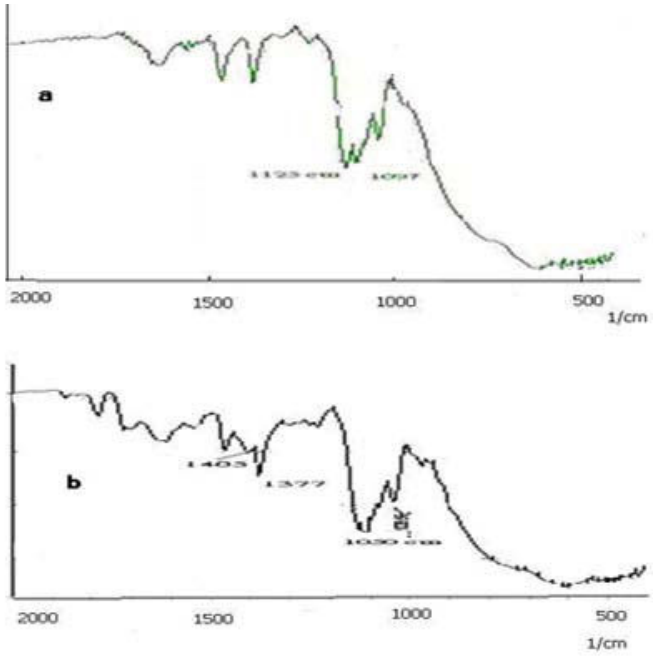


Fig. 4 a- Titanium –gel, b-TCPP doped in gel

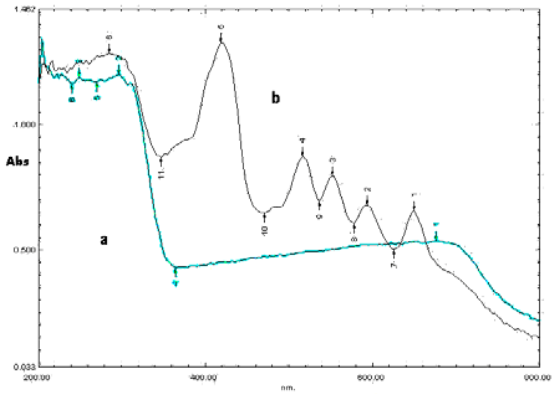


Fig. 5 Absorption spectra of H_2TCPP, a-before b-after sol-gel polycondensation

The aggregates are characterized through a new and sharp optical absorption band (J-band), which is shifted to longer wavelengths with respect to the intense absorption band of the monomers at about 400 nm (the Soret band), followed by several weaker absorptions (Q-bands) at higher wavelengths from 450 to 700 nm.

C. SEM images

The SEM photographs in Fig.6 show titanium-gel (a,b) and Titanium gel with doped TCPP, these pictures shows that TCPP successfully doped in Titanium gel.

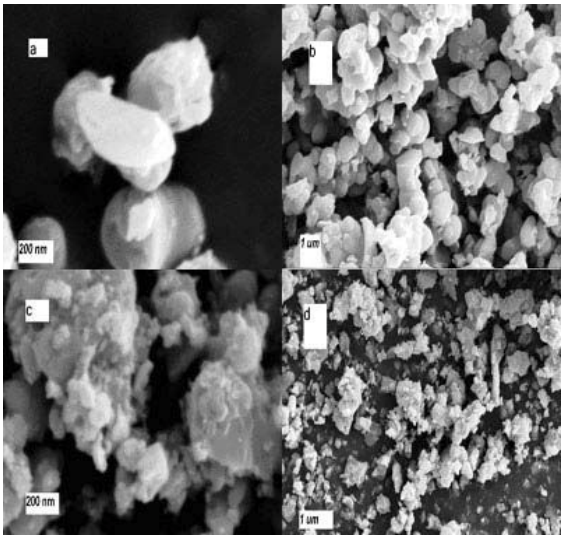


Fig. 6 (a,b) before and (c,d) after sol-gel polycondensation of H_2TCPP in Titanium gel

Titanium matrix is characterized through IR , UV and SEM spectrums .To fix porphyrin in gels,it is necessary to substitute an appropriate reactive group in the periphery of the macrocycle, to make them more soluble in water or alcohols. The more frequently employed substituents are: $–SO_3^-$, $–Na^+$, –COOH and pyridinium salts.

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