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FREE-BASE CARBOXYPHENYL PORPHYRIN /TIO2 COMPOSITE POROUS FILMS FOR THE OPTICAL DETECTION OF NO2

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Summary: Porphyrins are a very interesting family of compounds with many applications in new technologies such as solar cells, photodynamic therapy or gas sensors mainly due to their chemical and physical properties. A wide range of substrates can be used as solid support for these molecules. Recently, the preparation of columnar TiO2 thin films by physical vapor deposition at glancing angles (GAPVD) has been developed and has attracted our attention because of their microstructure, with large and open pores, making them very accessible to the incoming molecules. These systems have been found to be ideal for the study of diffusion processes of porphyrins. ,

In this work we have studied the anchoring effect of free-base carboxyphenyl porphyrins to TiO2 microstructured columnar films and its influence on NO2 sensing. In particular we have investigated 5-(4-carboxyphenyl)10,15,20-triphenyl-21H,23H-porphyrin (MCTPP); 5,10,15,20-tetrakis(4-carboxyphenyl)-21H,23H-porphyrin (p-TCPP); and 5,10,15,20-tetrakis(3-carboxyphenyl)-21H,23H-porphyrin (m-TCPP).

UV-vis spectra of these three composite films have shown that m-TCPP/TiO2 films are the most stable, and presents less aggregation than the other porphyrins, with a main peak at the same wavelength as its monomer in solution. Binding to TiO2 thin films were corroborated by FTIR and it showed that m-TCPP is bound through its four carboxylic acid groups, while p-TCPP is anchored by only one or two of these groups. MCTPP, given its structure, can only be bound to the TiO2 by one carboxylic acid. This kind of binding allows p-TCPP and MCTPP to interact (face to face) with other molecules causing aggregation due to $\pi-\pi$ interaction. This effect is greatly reduced by the more fixed anchoring of m-TCPP, which enhances the stability of its films. When exposed to NO2, MCTPP/TiO2, p-TCPP/TiO2 and m-TCPP/TiO2 thin films suffer important changes in their UV-vis spectra, which demonstrate that porphyrins have an extraordinary potential to be used as selective sensors for the detection of NO2, with fast and intense responses, being m-TCPP the best candidate mainly due to the higher stability of its films.

Moreover, concentration-dependent responses has been found when m-TCPP/TiO2 composite films are exposed to low concentrations of NO2 confirming the potential of this material as NO2 sensor.