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# Gas sensitivity of the surface potential of hybrid porphyrin-ZnO nanorods

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**Abstract**

In this paper we study the sensitivity to volatile organic vapors of the surface potential of metalloporphyrins coated ZnO nanorods. The hybrid material has been growth with an original method based on the direct addition of metalloporphyrins to the hydrothermal precursor solution. The resulting film shows a complete coating of the ZnO surface expected to improve the photovoltaic characteristics. The chemical sensitivity of the surface potential has been measured in dark and in white light illumination. For sake of comparison, the hybrid material has been compared with those obtained from a casting coated porphyrin functionalized ZnO nanorods. Results show that the material preparation strongly influences the sensor properties, and in case of the hybrid material the illumination with visible light elicits an increase of the sensor response that is proportional to the ability of the volatile compound to donate electrons.



*keywords*: ZnO nanorods; porphyrins; Kelvin probe

## 1. Introduction

It has been recently shown that the conductivity of porphyrins coated ZnO nanorods is influenced both by adsorbed molecules and visible light and that the exposure to visible light enhances the gas sensitivity [1]. The development of nanoporous or nanostructure material to maximize surface/volume ratio is fundamental in many fields like photovoltaic application and chemical sensors. Nevertheless, if the solar

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or chemical sensitive dye coverage is not uniform and complete this effort could result vain. In this context, casting solvent coating does not provide a complete coverage of the ZnO surface as a consequence the potentialities of the porphyrin-ZnO material are not fully exploited. Herewith, a novel hybrid material preparation where porphyrins are added to the precursor solution of the hydrothermal method growth is introduced (Fig. 1). Here a zinc tetraphenyl porphyrin functionalized with four sulfonate groups (ZnTPPS) has been tested. Afterwards, the sensing properties of the surface potential are investigated. Surface potential is an important parameter for chemical sensors that is exploited in many solid-state sensors such as ChemFETs. For sake of comparison, the surface potential of a casting coated Zn[illegible] ith a car[illegible] d for its [illegible] the sur[illegible] the cor[illegible] ating ele[illegible] esses suc[illegible]

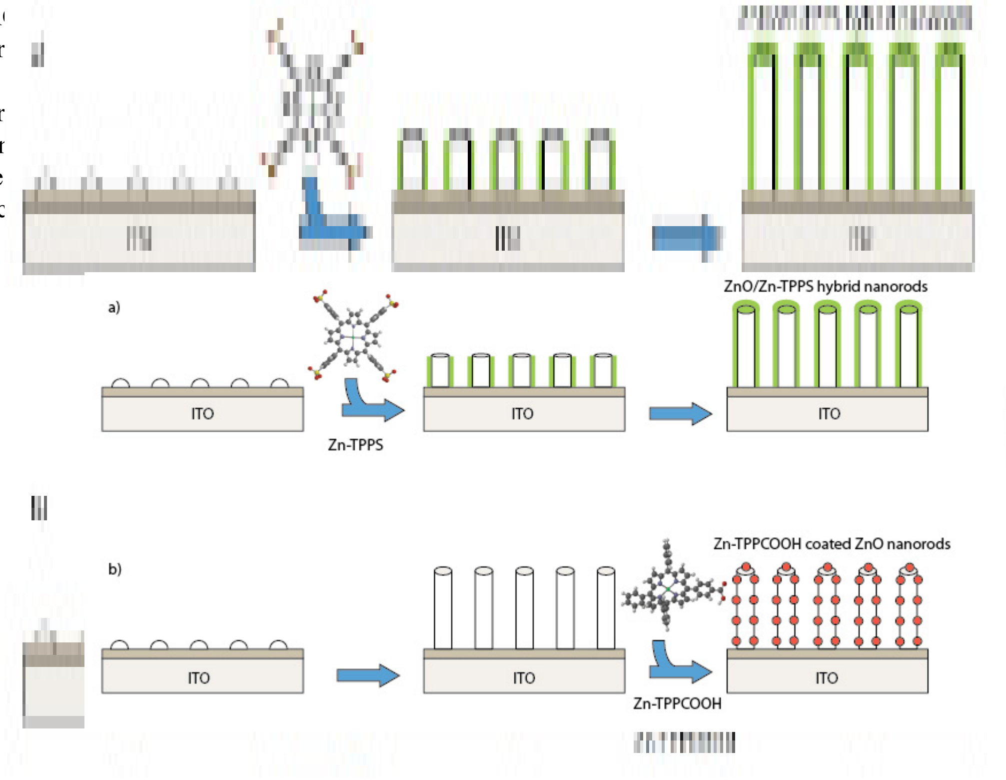


Fig. 1: Sensing layers fabrication. a) The porphyrins are added to the ZnO precursor solution. b) A porphyrin layer is deposited after the nanorods formation.

## 2. Experimental & Results

Hybrid material was obtained adding 0.5 mM of zinc tetrasulphonatephenyl porphyrin (ZnTPPS) to the standard precursor solution used for hydrothermal synthesis of ZnO nanorods. For comparison a sample was prepared coating with 0.1 mM solution of [5-(4-carboxyphenyl)-10,15,20-triphenylporphyrinate]Zinc (ZnTPPCOOH) the surface of normally produced ZnO nanorods. Recipes for the preparation of nanorods are available in ref. 1.

The morphology of the samples has been investigated with TEM and selected area electron diffraction (SAED). Fig 2a and fig. 2b show the results of ZnTPPS coated ZnO and Fig. 2c and 2d show the same analysis on ZnTPPCOOH coated ZnO. Porphyrins added after the ZnO growth form a sparse pattern of spots while a compact coating is obtained when porphyrins are added to the precursor solution.

The gas sensitivity of the surface potential of the two porphyrin-ZnO materials was tested exposing the materials to various concentrations of amines (trimethylamine, triethylamine and dipropylamine) and alcohols (ethanol, propanol, and butanol). The surface potential was measured with a Kelvin probe both in dark and under the visible light produced by white LED.

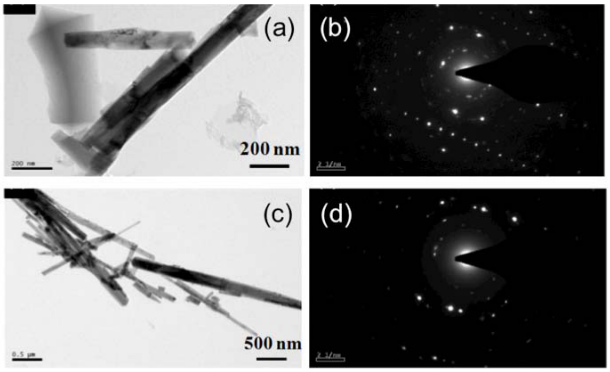


Fig. 2: TEM and SAED images of hybrid material (a and b) and casting coated material (c and d).

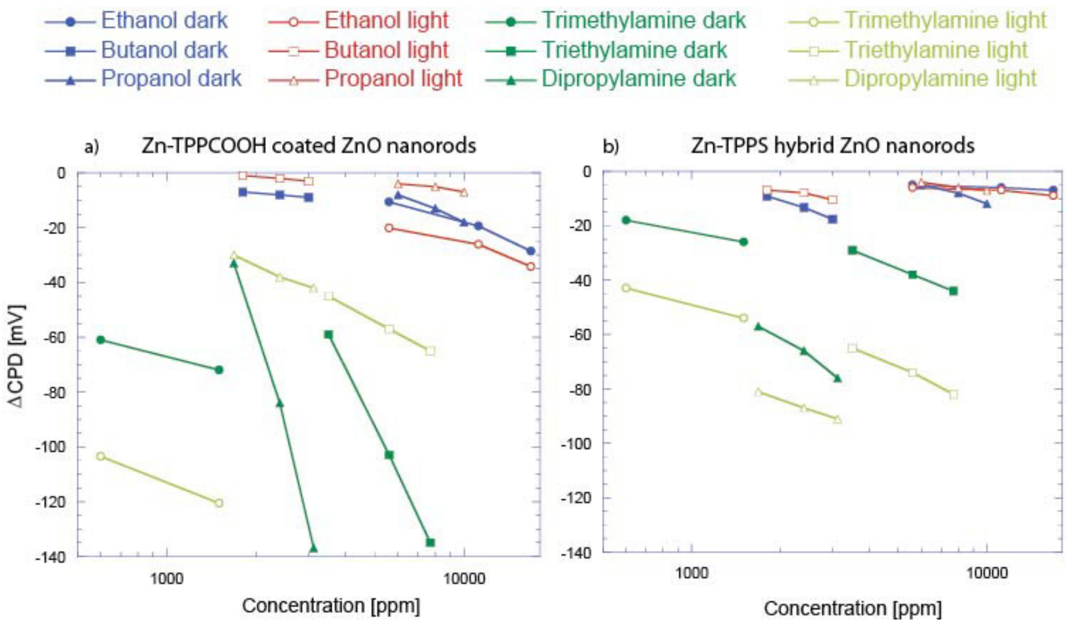


Fig. 3: a) CPD shifts for casting coated material for the various VOCs and different light conditions. Light induced signal increases are observed only for trimethylamine. For the other amines an inhibition of the response is found. b) CPD shifts for hybrid material for the various VOCs and light conditions. A net increase of signal is observed in presence of light for all the amines. To accommodate the large concentration range, in both figures the x axis is plotted in logarithm scale.

Fig. 3a and Fig. 3b show the CPD shifts as a function of the VOCs concentrations. In all cases, the largest signals are observed for amines, as expected considering their electron-donor property.

In the case of the hybrid material (ZnTPPS) the exposure to light enhances the response to amines while it is only barely visible in the case of alcohols. In casting coated material (ZnTPPCOOH) the exposure to light increases the signal only in case of trimethylamine, and noteworthy, a signal decreases is observed for the other amines. Coordination is expected to rule the interactions between VOCs and ZnTPPS and ZnTPPCOOH, then it is reasonable that the exposure to light enhances the sensor response towards the compound characterized by a strong Lewis basicity, trimethylamine in this case. On the other hand, the opposite behavior shown by ZnTPPS and ZnTPPCOOH with respect to the other amines suggests the importance of the organic layer morphology. These differences can be better captured by the biplot of the Principal Component Analysis (PCA) of the whole data set (Fig. 4) where ZnTPPS and ZnTPPCOOH lie, indipendently from the light conditions, on different sectors of the principal components plane.

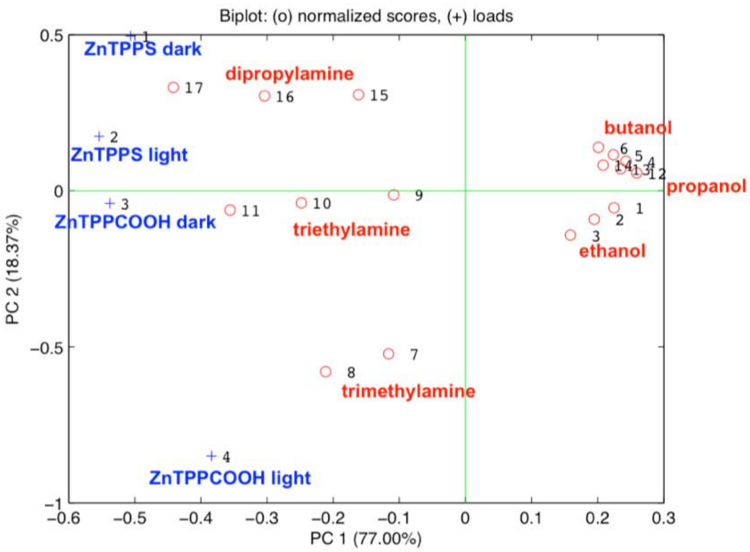


Fig 4: Biplot of the PCA calculated on the whole measurements. The scores (plotted in red) shows the separation between amines and alcohols along PC1. Along PC2 the separation of the individual compounds of each category is obtained. Loadings (plotted in blue) show the different behavior of ZnTPPCOOH in light evidencing the increase of the response to trimethylamine and the inhibition of the response towards the other amines.

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