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Development of Gas Sensor Array based on Phthalocyanines Functionalized TiO_2/ZnO Heterojunction Thin Films †

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† Presented at the Eurosensors 2018 Conference, Graz, Austria, 9–12 September 2018.

Published: 20 November 2018

Abstract: Gas sensing properties of diverse phthalocyanines functionalized TiO_2/ZnO heterojunction thin films were investigated respect to a number of volatile organic compounds (VOCs) in both dark and light conditions. These studies showed that influence of heterojunction along with functionalization alter the optical properties and gas sensing of sensors. Results show that each sensor exhibits a different pattern of relative sensitivity, and this feature can be used to discriminate among a wide range of VOCs.

Keywords: spray pyrolysis; heterojunction thin films; phthalocyanines; gas sensor array; VOCs

1. Introduction

Currently, gas sensor technology has numerous potentialities for on-site detection of malodors, particularly expanding an interest over clinical application, increasing the possibilities for diagnose the specific disease by analyzing disease specific VOCs present in exhaled breath. Achieving high performance in metal oxide based gas sensor array are exceedingly crucial. Moreover, it is found to be very challenging for researchers. However, recent studies showed that the performance of gas sensors can be enhanced towards specific gases by means of organic molecules functionalization of metal oxides surface [1]. In this work, an array of four sensors made up of TiO_2/ZnO heterojunction thin films was fabricated by spray pyrolysis technique and then functionalized with different zinc phthalocyanines carrying different functional groups (Figure 1) [2].

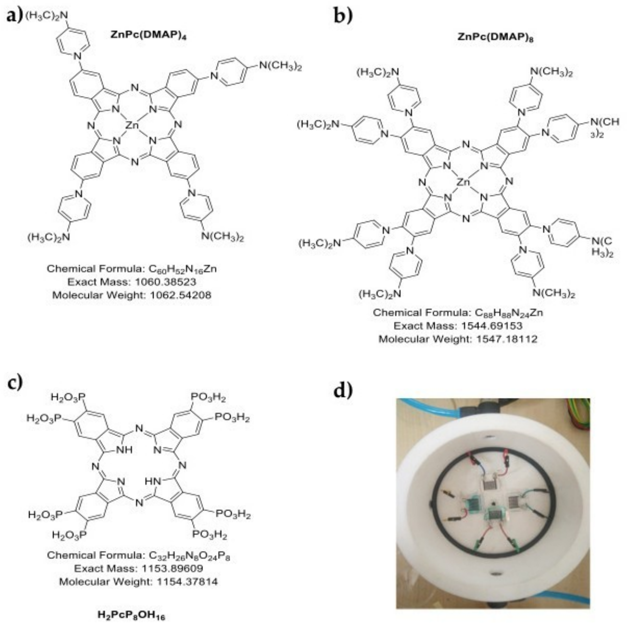

Figure 1. Structures of (**a**) Pc(DMF)$_4$, (**b**) ZnPc(DMF)$_4$, (**c**) ZnPc(DMF)$_8$ respectively, and (**d**) gas sensor chamber with four sensors.

2. Materials and Methods

Required chemical reagents and solvents such as titanium tetra isopropoxide, zinc acetate dihydrate, ethanol and methanol were purchased from sigma Aldrich and Sisco research laboratories. 0.2 M of Titanium tetra isopropoxide was added in 40 mL of ethanol solvent under constant stirring at room temperature for 3 h by using magnetic stirrer. As a result milky solution was obtained, which is followed by adding glacial acetic acid drop by drop during vigorous stirring of solution until it become transparent. The same procedure was repeated for preparation of ZnO solution, herein 0.2 M of zinc acetate dehydrate was added in 40 mL of methanol solvent under constant stirring for 3 h by using same magnetic stirrer. Initially, thin film of TiO_2 was deposited on quartz substrate endowed with interdigit electrode from previously prepared precursor solution of TiO_2 by spray pyrolysis method which is followed by depositing ZnO film using same procedure. One sample was left without functionalization taken as pure TiO_2/ZnO to make gas response comparison with remaining three samples which are functionalized with metal free phthalocyanine group with four functional group of Dimethylaminopyridine(DMAP), phthalocyanine group with zinc metal coordination and four functional group of Dimethylaminopyridine(DMAP), phthalocyanine group with both metal coordination and eight functional group of DMAP, which are labelled as Pc(DMF)$_4$, ZnPc(DMF)$_4$, ZnPc(DMF)$_8$ respectively. Finally to do gas sensor measurement, all the four sensor were placed in air tight gas chamber setup and it is tested with 14 different VOCs. The response of each sensors were recorded simultaneously by measuring change in resistance via Keysight Datalogger 34972A. Figure 1d shows the gas chamber setup.

3. Results and Discussions

Figure 2a shows TiO_2/ZnO heterojunction funtionalized with different pthalocyanines. Absorption peaks corresponding to ZnO is observed in the UV region (Figure 2b). The inset shows the peaks in the visible region and it proves that functionalization with pthalocyanines made sensors to be sensitive in visible light region. The conductivity of sensors was measured during the exposure to various concentration of VOCs representative of different chemical families in dark and light conditions. Results show a linear response for a wide range of concentrations of VOCs (Figure 3).

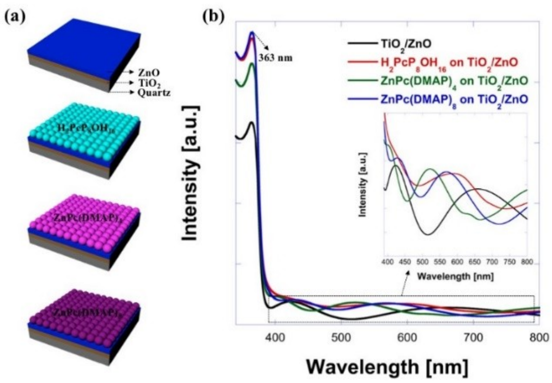

Figure 2. (**a**) Schematic illustration of phthalocyanines functionalized TiO_2/ZnO heterojunction. (**b**) UV-Vis absorption spectra of bare and various phthalocyanines functionalized TiO_2/ZnO heterojunction.

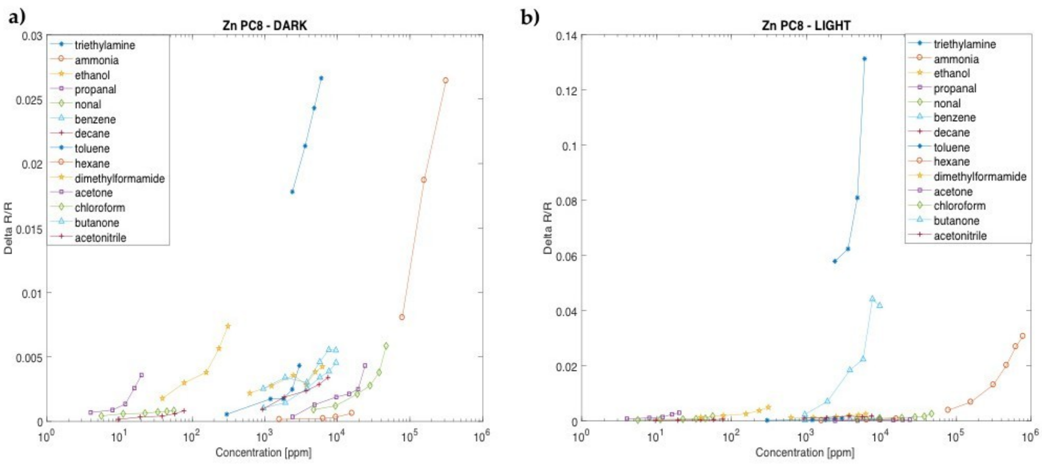

Figure 3. Response curves of Zn-Pc8 coated sensor measured in dark and light conditions. The increase of response is observed in particular for triethylamine and benzene. Concentrations are plotted in a logarithmic scale to accommodate the concentration range spread due to the different saturation pressures.

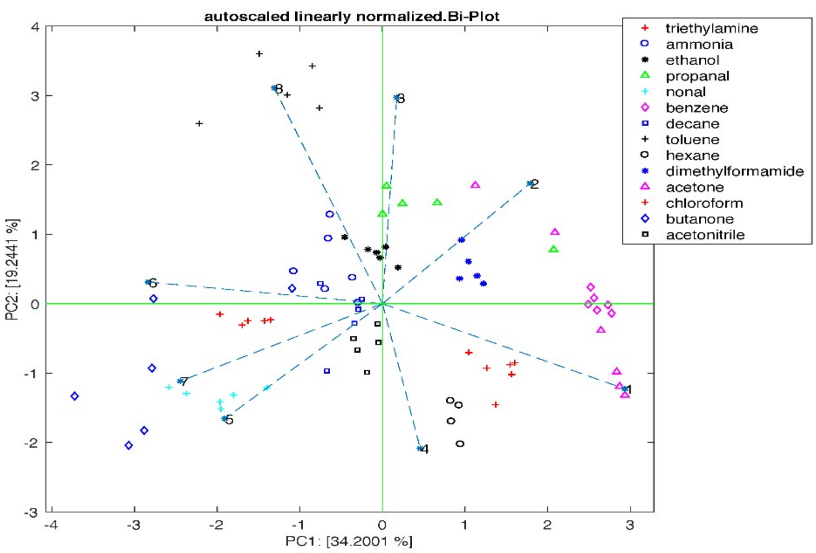

Figure 4. PCA scores and loads plot. A clear separation is observed for almost all the VOCs. Loads show the each sensor differently contribute to the PCA representation. Data were linearly normalized to remove the part of the dataset correlated with the concentration.

Furthermore, the exposure to light modifies the response increasing the sensitivity of donor species such as triethylamine. The different behavior of sensors, due to both the characteristics of the functionalizing unit and the light condition, are sufficient to endow the array with the necessary combinatory selectivity to identify the different VOCs disregarding their concentration.

4. Conclusions

TiO_2/ZnO heterojunction functionalized with three different pthalocyanines based sensors have been fabricated. Optical studies suggest that the functionalized molecules did not alter TiO_2/ZnO as well as their spectral features. Conductivity studies on sensors under exposure of 14 various VOCs both in light and dark conditions have shown that these hybrid sensors are sensitive towards donor species like triethylamine. Also, PCA studies have shown that the sensors can able to distinguish VOCs, clearly. Overall, our investigations have suggested that the fabricated sensor array can be utilized in clinical diagnosis.

Author Contributions: Y.S. and C.D.N. conceived and designed the experiments; J.B.J.H. and S.M. fabricated sensors; J.B.J.H. performed the gas sensor experiments; V.N. synthesized pthalocyanines; Y.S., C.D.N., G.M., and S.V.J. analyzed the data; Y.S., C.D.N., and S.V.J. wrote the paper.

Acknowledgments: Yuvaraj Sivalingam acknowledges the major financial support from the DST-SERB, New Delhi, India (File No.: ECR/2017/001218).

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