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Research paper

Development of gas sensor array based on phthalocyanine functionalized bilayer TiO_2:ZnO thin film towards l iver disease detection

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Abstract

Currently, Gas sensor technology has numerous potentialities for in site detection of malodors, particularly expanding an interest over clinical application, increasing the possibilities for diagnosis specific disease by analyzing disease specific volatile organic compounds present in Exhaled breath. Achieving a high performance in metal oxide based gas sensor array are exceedingly crucial and moreover found to be very challenges for researchers. But recent studies showed with the aim of performance of gas sensor can be enhanced towards specific gases by means of organic molecules functionalization over sensing material of sensor. So Herein, an array of four sensor made up of bilayer TiO2: ZnO Thin film was fabricated by spray pyrolysis method and later on functionalized them with different phthalocyanine organic molecules vary with functional groups and metal ion. These sensor array was tested in various concentration of different volatile organic compounds such as methyl ethyl ketone, Triethylamine decane, ethanol and propanol, those are considering as novel gases remarkably found to be present quiet higher in amount in exhaled breath of liver disease patients. Results showed that the distinct character of each phthalocyanine organic molecules manipulate sensor response which are adequate headed for facilitate the discrimination of volatile organic compounds which is good enough to cover volatile organic compounds present in human breath. These outcomes may perhaps gain interest to further optimize and validate the gas sensor array for real time application towards early detection of liver disease as it is one of the most prevalent disease and the fifth most common causes of death in India

Key words: *Metal oxide sensor, phthalocyanine, Volatile organic Compounds, Gas sensor array.*

1. Introduction

As per world organization, liver disease is the tenth most common cause of death in India and around 10 lakh patients of liver disease are diagnosed consistently every year. Some statistics postulates that liver cirrhosis is the 14th leading cause of death in the world and also might a chance to be those 12th heading reason for deaths in the world by 2020 [1]. Alcoholic liver disease (ALD) and Nonalcoholic fatty liver disease (NFLD) are serious cause of abnormal liver function and ranges from simple hepatic steatosis to steatohepatitis, liver cirrhosis, and hepatocellular carcinoma [2]. The former is due to excessive intake of alcohol and latter is due to excessive intake of food which leads to metabolic syndrome in obese individuals. With respect to numerous disease, liver disease can be mortal if left untreated. So it is inevitable for early detection of liver disease.

As many years, Liver biopsies remain a gold standard method for liver disease detection. Since it is invasive, inconvenient and impractical to perform liver biopsies on all suspected patients, noninvasive procedure comes into picture and has high demand towards liver disease detection. In case of blood test, alanine transferase levels are found to be normal in some liver patients which leads to false diagnosed results. [3][4]. Imaging methods such as ultrasonography (US) and computed tomography (CT) are widely used for visualize and diagnosed fatty changes of liver, but recent studies reported that the sensitivity of these imaging techniques is not good enough (53.3% to 66.6%) to diagnose mild steatosis [4,5].

Exhaled breath analysis is a promising non-intrusive approach to analyze specific volatile organic compounds present in human breath of patients, act as an indicator for specific disease, which in turn reflects the status of one's health condition [6]. Exhaled breath analysis has possibility not only to diagnose disease as well as it enables to assess its severity, progression and response to treatment. Coated quartz crystal microbalance [7], Ion flow tube mass spectrometry [8], polymer-coated surface acoustic wave sensors [9], laser absorption spectrometry [10], Gas chromatography with mass spectrometry(GC-MS)[11,12] and infrared spectroscopy[13], sensors have been used for diagnose specific biomarkers related to respective metabolic disorders. However, these analytical methods have certain limitation of being highly expensive, tedious procedure, required trained operators and also required pre-concentration of biomarkers [14]. So nanomaterials based sensors has an attracted a lot of attentions in a field of clinical diagnosis due to its large surface- volume ratio and unique chemical, optical and electrical properties to enhance the sensitive and response of the sensor. Especially metal oxide semiconductor (MOS) based chemo resistor are most commonly used sensor owing to its advantage of being inexpensive, long life period and fast response, despite of its few drawbacks like high power consumption and less sensitivity and specificity to specific VOC compared to other analytical techniques [15]. Physical quantities such as temperature and intensity of light has greatly influenced on enhancing the gas sensing properties of metal oxide materials. Furthermore, many studies have proved that the performance of metal oxide semiconductor materials can also be improvised by functionalized with appropriate organic molecules which in turn leads to enhancement of photovoltaic properties and catalytic properties due to its own unique properties of organic molecules [16] [17]. Since phthalocyanine are extremely suitable as a chemically sensitive material due to its strong photophysical properties [18], we have been intrigued to investigate the sensing qualities of phthalocyanine coated bilayer TiO_2: ZnO thin film. Thus in this paper, we have investigated the sensing properties of different phthalocyanine group coated - an array of four bilayer TiO_2:ZnO which was deposited on substrate endowed with interdigit electrode for resistivity measurement towards liver disease detection by testing sensitivity of senor array towards five volatile organic compounds such as, methylethyl ketone, triethylamine, decane, ethanol and propanol which are specific volatile organic compounds related to liver disease and found to be present more prominent in exhaled breath of patients affected by liver disease [6,19].

2. Experimental Procedure

Preparation of precursor solution for TiO_2 and ZnO

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, used in this work. 0.2M of Titanium tetra isopropoxide was added in 40 ml of ethanol solvent under constant stirring at room temperature for 3h 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 solution. The same procedure was repeated for preparation of ZnO solution, herein 0.2 M of zinc acetate dehydrate was added in 40ml of methanol solvent under constant stirring for 3 h by using same magnetic stirrer [20].

Deposition of TiO2:ZnO thin flim

Prior to deposition, quartz substrates were cleaned with deionized water, ethanol and isopropanol in ultrasonicator for 30 mins at 50°C subsequently [21]. Finally, the cleaned substrate was once again rinsed with deionized water and dried it in hot air oven. Silver interdigit electrode was patterned on cleaned quartz substrate by using screen printing method. 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 [20]. The spray pyrolysis set up was operated at 3 psi pressure which was made to spay precursor solution on substrate at 450°C in form of mist from nozzle bulb which was kept at 45° angle to substrate holder above which Quartz substrate was placed to be coated. The substrate temperature can be varied based on requirements. The distance between nozzle and substrate was 30 cm. The deposition time was fixed as 1 sec for every 30 sec intervals. Then, the coated thin film was allowed to cool till it reach room temperature. Later on, its functionalized with phthalocyanine group with different combination of functional group and metal ion. One sample was left without functionalization taken as pure TiO_2:ZnO to make gas response comparison with remaining 3 samples which are functionalized with metal free phthalocyanine group with 4 functional group of Dimethylaminopyridine(DMAP) , phthalocyanine group with zinc metal coordination and 4 functional group of Dimethylaminopyridine(DMAP), phthalocyanine group with both metal coordination and 8 functional group of DMAP, which are labelled as $Pc(DMF)_4$, $ZnPc(DMF)_4$, $ZnPc(DMF)_8$ respectively. Fig.1 shows experimental detail for sensor fabrication.

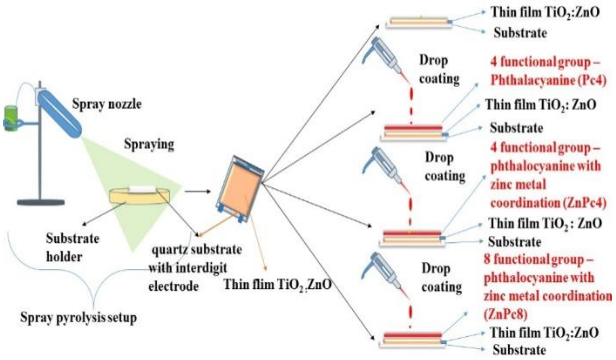


Fig.1. Experimental procedure

Gas Response Measurement

To start up with gas measurement, all four sensors were placed in air tight gas chamber setup and tested with different gases by injecting gas vapor at different concentration via inlet of gas chamber setup by means syringe. This is followed by using purging system to purge out testing gas via opening the outlet of gas chamber, which enables for recovery of sensor, bringing back to its base resistance and make it ready for next set of gas response measurements with other target gas. The response of each sensor were recorded simultaneously by measuring change in resistance via Agilent data logger 3497A0. Fig.2 shows gas chamber setup for gas response measurement. The vapor pressure for each gas were calculated by antoine equation at room temperature. Then ppm was calculated by using below formula,

PPM= [vapor pressure of gas at room temperature /total atmospheric pressure] *1000000

The gas response for testing gases were measured by

Sensor response = (Ra-Rg)/Ra

Where Ra and Rg is resistance of sensor in air and target gas.

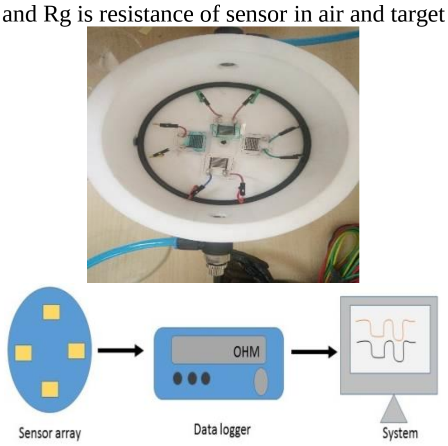


Fig.2. Gas chamber set up for static measurements (a) gas sensor array (b) schematic diagram of measurement setup

3. Results and Discussion

The crystallinity structure of bilayer thin film TiO_2: ZnO was examined using Xray Diffraction (XRD). Fig.3 shows XRD pattern of bilayer thin film of TiO_2-ZnO. Peaks at 34.4°,36.5°,47.7°,63.1° corresponds to crystal planes of (002), (101), (102), (103) that are ascribed to ZnO under JCPDS card no - 75-1526 whereas peaks at 44.6° assigned to (210) diffraction peak of TiO_2, which confirmed rutile phase of TiO_2 according to JCPDS card no – 88-1174. Diffraction peaks of ZnO were more strong with high intensity than TiO_2 as ZnO layer was top layer coated over TiO_2 layer. Further, most of the diffraction peaks in XRD were sharp, which indicated high crystallinity structure of TiO_2 and ZnO.

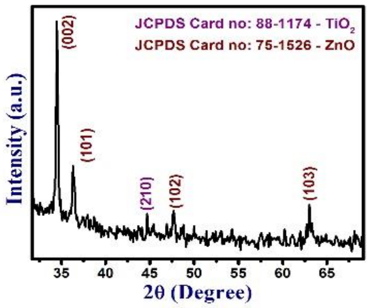


Fig.3. XRD pattern of bilayer TiO2: ZnO

Fig.4a) shows typical gas response of all four sensors for triethylamine gas in different ppm concentration. Fig.4b) depicts an individual gas response of $Pc(DMAP)_4$-TiO_2/ZnO triethylamine for specified range of ppm concentration. Since all volatile organic compounds are indicated by their saturated vapor pressure (i.e.) tendency to evaporate at standard temperature and pressure, each gas has different vapor pressure at room temperature. So corresponding ppm concentration obtained from those vapor pressure will also be varying for different gases. In this work, concentration range is taken between 8% to 0.8% of saturated vapor pressure for all gases which is being used for static gas measurements. Fig.5 shows linear fit response curve of all four sensors to five volatile organic compound. Thus, it shows a steadiness of the sensor as it is profoundly depending on the consistency in the linear variation of the sensor

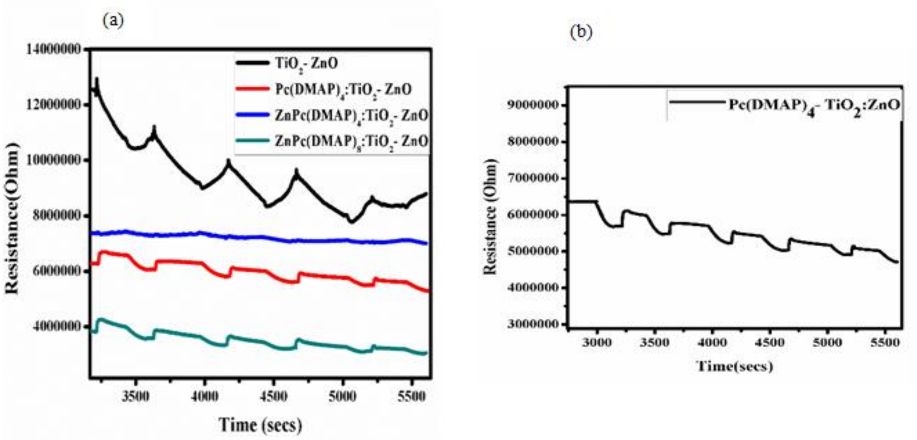
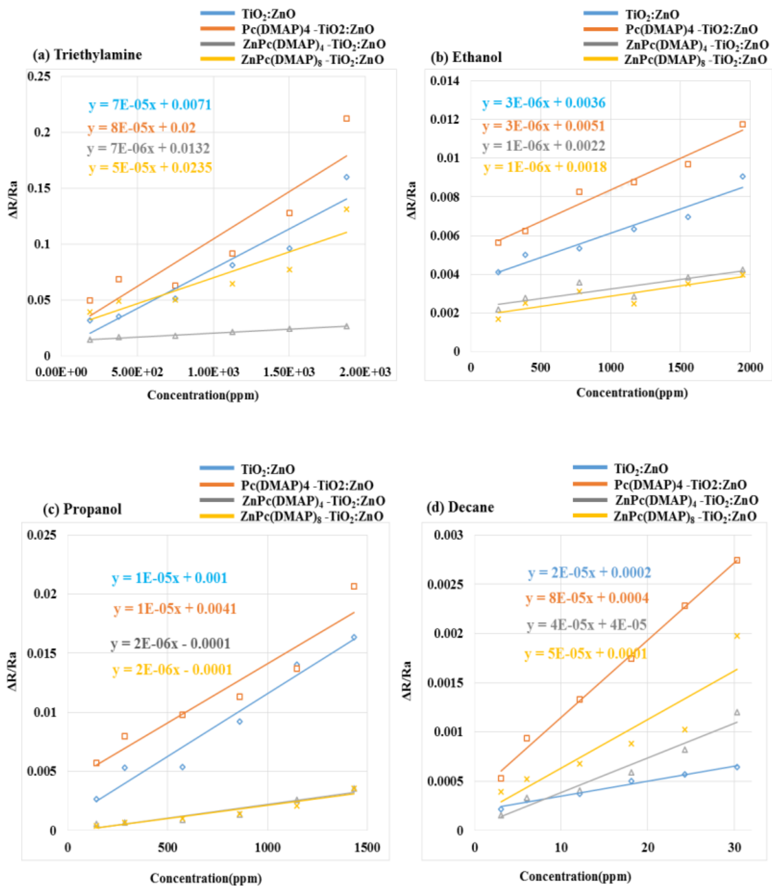


Fig.4. Typical response of (a) all four sensors and (b) single sensor of $Pc(DMAP)_4$-TiO2: ZnO for Triethylamine gas of specified range of concentration from 1900 to 190 ppm.



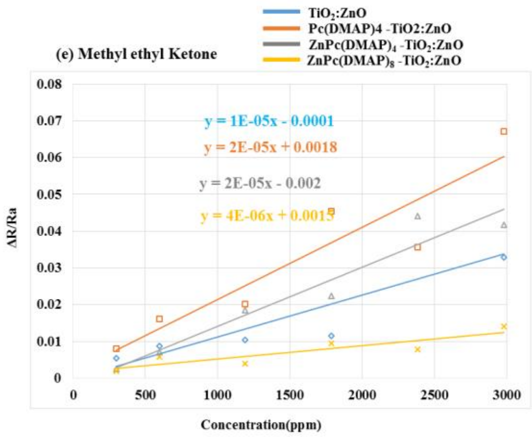


Fig.5. Linear fit response curve of four sensors for five volatile organic compounds (a) Triethylamine (b) Ethanol (c) Propanol (d) Decane (e) Methyl ethyl ketone at different concentration range

Fig.6 shows sensitivity of each sensor for five volatile organic compounds. From above observation, bilayer thin film TiO_2: ZnO shows reasonable response for triethylamine compared to other volatile organic compounds. The reason for this high response for triethylamine gas may be due to presence of nitrogen atom, tends to make bond with bilayer TiO_2: ZnO. Additionally, the presence of Silver interdigit electrode in bilayer TiO_2: ZnO thin film beneficially increase the catalytic activity of the sensor as it has been reported in relevant literature survey [22].

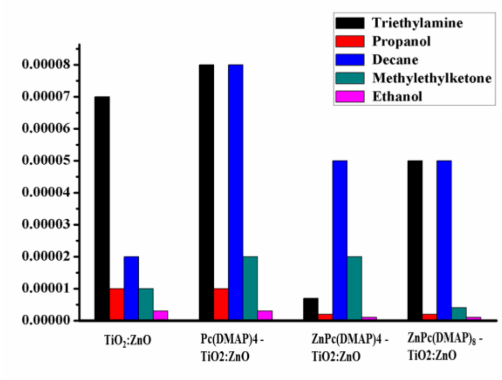


Fig.6. Sensitivity of each sensor under static gas measurement when exposed to triethylamine, proponol, methyl ethyl ketone, Decane, ethanol.

In case of sensor functionalized with $Pc(DMAP)_4$ shows a strong response towards triethylamine gas and Decane with respect to other sensors. This may be due to presence of functional group (DMAP) which is being anchored on the surface of bilayer film, act as mediator to transfer electron from triethylamine (electron donor) to bilayer surface in good enough to enhance response towards electron donor species as well as it enables long chain alkanes group of Decane to interact with sensing material to enhance response towards decane where as in case of sensors functionalized with Zinc metal coordination $ZnPc(DMAP)_4$ amine group coordinate with metal ion might not be strong enough to promote electron transfer from phthalocyanine to bilayer. On the account of this, relatively less response has been observed for trimethylamine gas compared to $Pc(DMAP)_4$ and $ZnPc(DMAP)_8$which is well agreed with recent study [16]. As an individual sensor functionalized with $ZnPc(DMAP)_8$ shows measurable response towards Decane as same as sensor functionalized with $ZnPc(DMAP)_4$ owing to increased number of functional group improved response despite of presence of metal ion but lesser than metal free functionalized sensor. But in case of sensor functionalized with $ZnPc(DMAP)_4$, no appreciable response has been observed for other gases except Decane. This may be due to presence of Zn metal ion counteract the function of functional group to promote electron transfer, make it available for interaction with bilayer TiO_2:ZnO sensing material. As a result of this, only bare sensitivity has been seen for other gases among functionalized sensors but slightly improved sensitivity towards methylethyl ketone has been seen, compared to TiO_2:ZnO and $ZnPc(DMAP)_8$ sensor. Thus, here comes a significant role of surface functionalization of organic molecules to enhance response towards specific gases.

4. Conclusion

Thus, four gas sensor array of bilayer TiO_2:ZnO functionalized with different phthalocyanine group has been synthesized and tested with five volatile organic compounds. Because of limitation of experimental facilities, it has been tested up to low concentration as 3 ppm. But by considering linear behavior of each sensor, it is seen that sensor is able to detect as low concentration as possible. Sine every senor has exhibited different pattern of relative sensitivity, it is good enough to discriminate wide range of volatile organic compounds, possible to cover VOC present in human breath. As our gas sensor array is able to detect and shows distinct response towards triethylamine, decane, methylethyl ketone, ethanol and propanol are considering as novel gases of liver cancer and nonalcoholic fatty liver disease, which is sufficiently cover liver disease associated VOC present in human breath. If gas sensor array is further optimized to improve the response for even lower concentration, ultimately it can be applicable for real time application to early detection of liver disease from exhaled breath.

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