Single-Walled Carbon Nanotube- Polyaniline/Poly Porphyrin Composite for Gas Sensing-A mini Review

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***Abstract-------P*olyaniline (PANI) / Poly porphyrin (tetraphenylporphyrin) composite due to their Physical, Chemical, and Optical property can be used as sensory material for gas sensor. The problem of poor conductivity can be resolve by using Single Walled Carbon Nanotube (SWNTs) which has excellent conductivity. In this paper we focuses on enhancement of Conductivity, Stability, Sensitivity, Selectivity and Electrical Properties by combining these two materials viz. Polyaniline and Tetraphenylporphyrin (TPP). We have used TPP as poly porphyrin. We can optimize the sensing performance of the sensor by varying the various synthesis parameters viz. dopant, concentration, temperature, thickness, etc. of SWNTs coated PANI/ TPP composite and by applying different electric charge per unit surface of the space.**

Keywords—Polyaniline (PANI); Poly Porphyrine; Tetraphynilporphyrin (TPP); Single Wall Carbon Nanotube (SWNTs)

I. Introduction

Chemical sensor consist of two element first active element as a sensory layer and second transducer element. Conducting polymers are organic polymers and has excellent electrical conductivity act as a sensory layer in most of the gas sensor [2]. Conducting polymers has various advantages such as high sensitivity, better response time and ease of operation at room temperature. The physical and chemical properties of conducting polymers can be changed by using different molecules of different dopants (acid/base). Some typical conducting polymer are shown in the Figure 1.

In the recent years all these conducting polymer has received great attention for various application such as gas sensor, vapor sensor, chemical sensor and biochemical sensor. Polyaniline [PANI] is one of oldest synthetic conducting polymer. Especially polyaniline [PANI] received much more attention when it combine with SWNTs, among all other conducting polymers because of its highly stable chemical structure and excellent chemical and electrical properties. SWNTs act as backbone for any sensing materials due to unique electrical and structural properties, it can be used in many application due to its high electrical mobility which reduces power consumption of the device. It act as transducer for gas sensor which provide electrical signal on absorption of gas molecule.

Porphyrins are a group of heterocyclic macrocycle organic compounds which has excellent chemical and optical properties as well as good chemical stability. The parent porphyrin is a porphin, and substituted porphines are called porphyrins. Porphyrin macrocycles are highly conjugated systems and consequently they typically have very intense absorption bands in the visible region and may be deeply coloured. Many porphyrins are naturally occurring; one of the best-known porphyrins is “heme”, the pigment in red blood cells, a cofactor of the protein haemoglobin. Porphyrin and metalloporphyrins has ability to interact with various chemicals due to its inner core metal ion structure which make them a great sensing material. In this paper we have been focusing on only Tetraphenylporphyrin (TPP) which resembles from porhyrins. The study of natural porphyrin is very complex due to their low symmetry and presence of polar substituent. Tetraphenylporphyrin is hydrophobic, symmetrically substituted, and easily synthesized, it can be easily dissolve in non-polar solvent. According to Ashok Mulchandani et.al. SWNT−poly(porphyrin) hybrid for volatile organic compound sensing applications in which the issue low conductivity due to porphyrin resolved by using SWNTs as a backbone for sensing materials [5]. Chemical structure of TPP is shown in Figure 2.

II. PANI Based Gas Sensors

A. Electrical Properties

PANI has simple doping/dedoping chemistry and its general formula is $[(\text{-B-NH-B-NH-})_m (\text{-B-N=Q=N-})_{1-n}]_m$ in which B denotes benzenoid ring and Q denotes quinonoid ring. PANI has three oxidation states, leucoemeraldine, fully reduced form (n=1), pernigraniline, fully oxidized form (n=0)

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and most attractive form which is used in most of the sensing material is emeraldine, partially oxidized (n=0.5) [4].

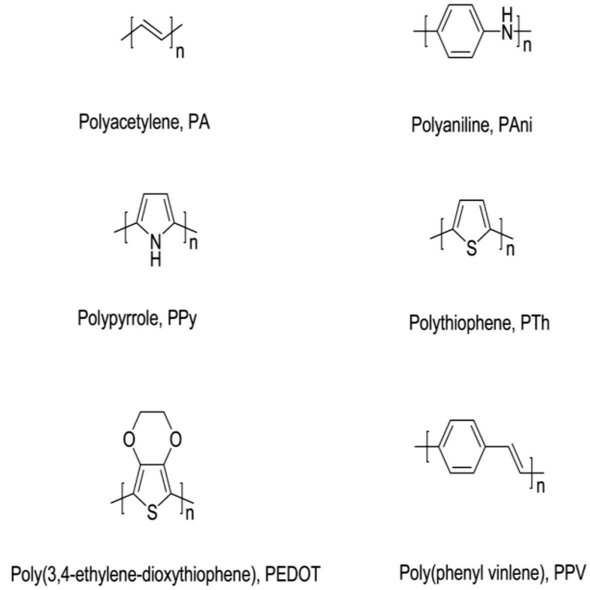

Figure 1. Chemical structure of some conducting polymer

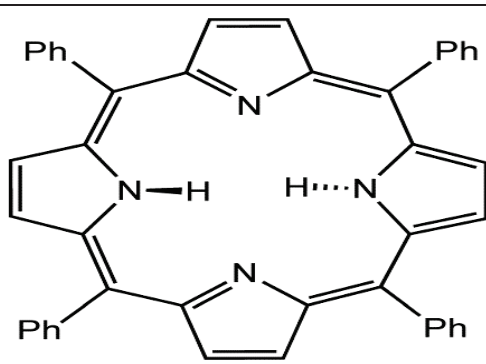

Figure 2. Chemical structure of Tetraphenylporphyrin

In conductive form emeraldine salt polyaniline is used where as emeraldine base is in insulating form. With the help of doping, electrical conductivity of polyaniline increases from emarldine base (σ<1x 10^{-10} S cm^{-1}) to emeraldine salt (fully conductive σ>1 S cm^{-1}) where σ represented as conductance of material [2]. Chemical representation of this conversion are shown in Figure 3 [2]. According to Maria Vittoria Russo et al. due to this switching property (between conducting and insulating) of PANI it is responsive to both acid/base and reducing/oxidizing compound like ammonia (NH_3), nitrogen dioxide (NO_2), hydrogen (H_2) and some volatile organic compound (VOCs) such as benzene, toluene and xylene [2]. Due to strong electrical polarization PANI is used as selective layer for chemiresistive sensing modality.

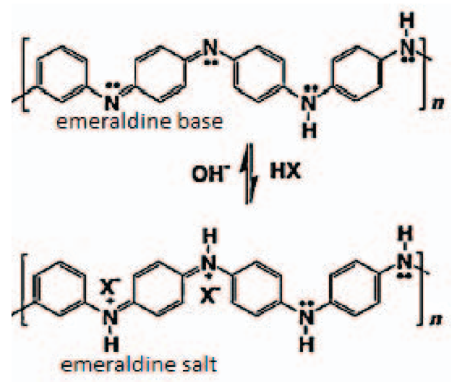

Figure 3. Chemical structure of conversion of emrealdine base to

Most of the researcher has used PANI as sensing material in 2D (thin film) but these Sensors has low sensitivity and poor recovery to resolve this issue SWNTs are used to prepare 1D structure. SWNTs has aligned in between two gold electrodes (3 micron) dielectrophoretically and then SWNTs functionalized with conducting polymer/ porphyrin [6, 11].

B. Sensitivity and Resistivity of PANI towards Gases Analytes

$$S = \frac{R}{R_0} = \frac{aC_0}{\sqrt{(K_m / D)}L} \tanh(\sqrt{\frac{K_m}{D}}L) \qquad (1)$$

The response of the PANI composite layer can be found by using equation (1). Where S is the response of the composite, C_0 is initial concentration of gas, L is diffusion length and D is diffusion constant. Sensitivity can be determined by a dimensional parameter m which is represented by equation (2).

$$m = \sqrt{(K_m / D)}L \qquad (2)$$

Sensitivity curve is shown in Figure 4.

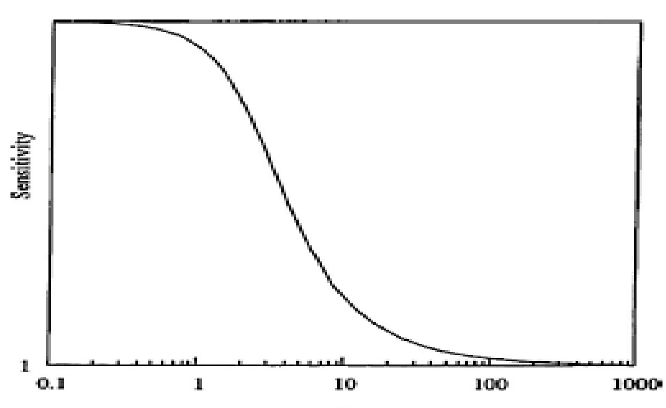

Figure 4. Generalized graph of the gas sensitivity of PANI in terms of adimensional parameter m= √(K_m/D) L

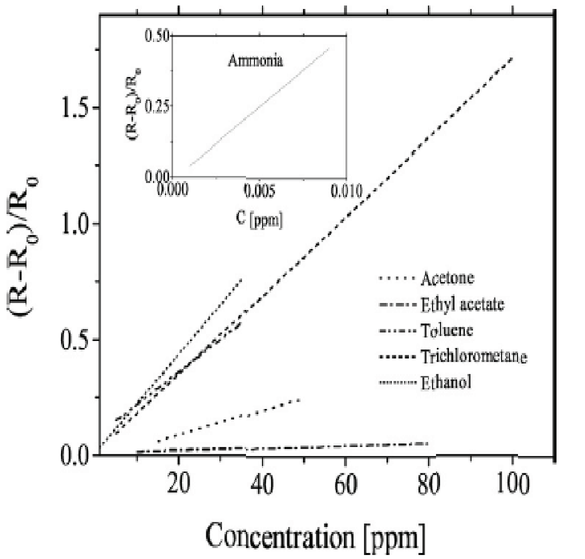

Figure 5. Resistivity graph of various volatile organic compound for PANI/SWNTs composite

Maria Vittoria Russo et al. shows the generalized normalized resistance vs concentration graph in Figure 5. And said due to high resistivity it is difficult to measure the gas. Hence resistivity should be in semiconducting range for PANI/SWNTs composite [2].

III. PORPHYRIN BASED GAS SENSORS

A. *Electrical Properties*

Surface modification of SWNTs with porphyrin can achieved through electropolymerization technique, according to Ashok Mulchandani et al. fabrication of SWNT−porphyrin hybrid nanostructure through electrochemical polymerization of tetraphenylporphyrin (TPP) on SWNT networks and evaluate the potential of this nanostructure as a chemiresistive sensor for acetone, as a model VOC, they have used solvent casting technique to fabricate the sensor where porphyrin and SWNTs connected to each other by π-π interaction without affecting the electrical property of SWNTs.[5]. Which is shown in Figure 6.

B. *Sensitivity and Resistivity of TPP/SWNTs towards Gases Analytes.*

Sensitivity of TPP/SWNTs is not as good as PANI/SWNTs because it has high resistivity, exposure of any gas molecules. According to M. D. Shirsat et al.[6] central metal ion of polyporphyrin play very important role in sensitivity and resistivity performance of the device they shows various resistivity graph of SWNTs/TPP composite material which shows that on exposure of gas the resistivity of device increases as the concentration of analyte increases and selectivity depend on the type of porphyrin used for the functionalization of SWNTs not depend on SWNTs. SWNTs work as backbone of the sensor for the signal transduction. Resistivity vs concentration graph is shown in Figure 7.

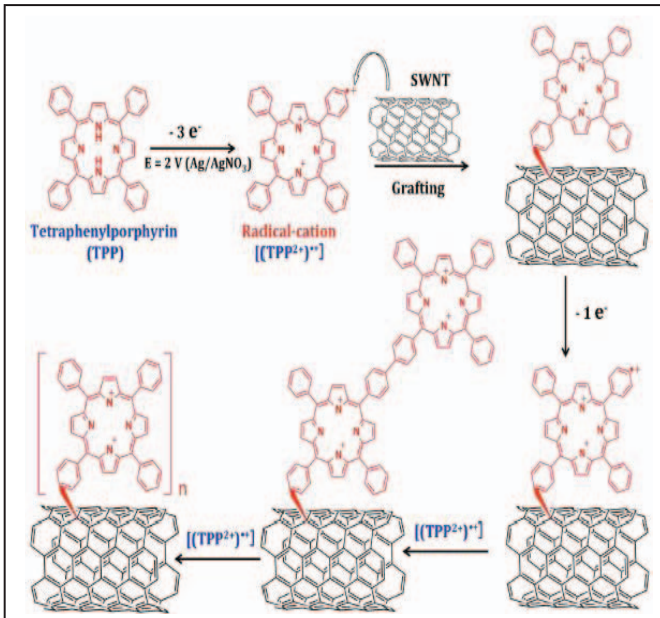

Figure 6. Electrochemical polymerization of TPP/SWNTs

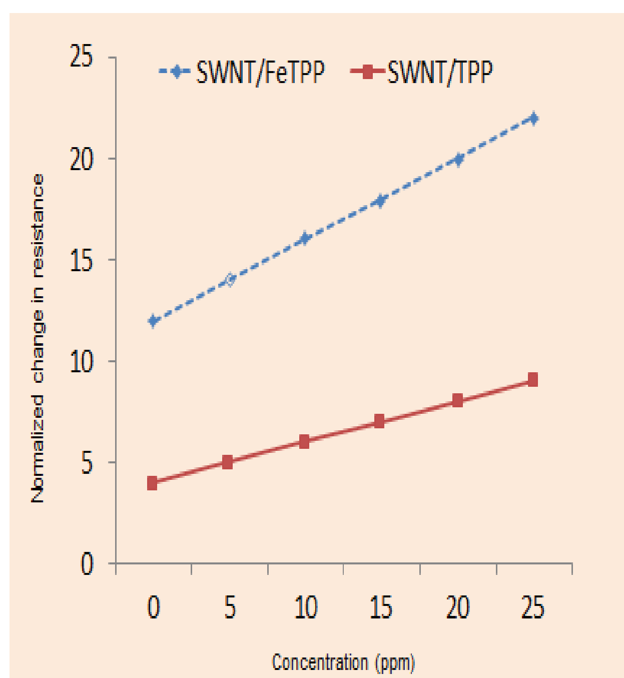

Figure 7. Resistivity graph of some SWNTs/TPP composite

CONCLUSION

This paper focused mainly on sensitivity and selectivity of the gas sensor. On the above discussion we can say that PANI based gas sensor has excellent environmental stability and sensitivity but it suffers from selectivity because it responses many gases like ammonia (NH_3), hydrogen (H_2), and some VOCs at the same condition. And porphyrin based gas sensor has good selectivity but poor sensitivity. Hence by taking composite of these two materials PANI/TPP with SWNTs we can improve both sensitivity as well as selectivity of the device and can be improve electrochemical properties as well.

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