SYNOPSIS of Ph.D. THESIS

on

CARBON NANOFILLERS BASED THIN FILMS FOR TOXIC GAS SENSOR APPLICATIONS

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1. Introduction:

There are various kinds of natural, chemical and artificial species available in our surrounding environment, some of them are very essential while others are more harmful or less. The essential gases/species like oxygen (O_2), nitrogen (N_2) and humidity should be maintained at sufficient level in global atmosphere while excess emission of hazardous or toxic gases can harm living atmosphere. In this regard, burning of fossil fuels (e.g. Coal, petroleum, and natural gas) is a major concern for global air pollution [1-3]. On burning, compounds containing carbon, nitrogen, and sulfur generate gaseous oxides by reacting with air. These toxic gases are harmful in living atmosphere in parts per million (ppm) or even parts per billion (ppb). Among these gases, increase emission of carbon dioxide (CO_2) and other greenhouse gases since the mid-20th century has been thought to be the cause of the increase in the average near-surface air and ocean temperature of the earth, a phenomenon known as global warming. In particular, CO_2 detection in ambient air has continued to be a challenge due to oxidizing stability of the compound and interferences from several species, such as nitrogen dioxide (N_2O) and carbon monoxide (CO). In many fields, such as industrial emission control, household security, and vehicle emission control, monitoring of CO_2 is mandatory. Further, a CO_2 sensor can be greatly beneficial to a wide range of applications, including breath and blood analysis for medical diagnosis [4-6], portable gas detector for personal protection and gas monitoring for climate control [7]. In view of safety regulation, a confined workplace should have CO_2 concentration level below 5000 ppm in 8 h average; even lower concentration can cause discomfort, headache, respiratory problem, and other sensitive health issues [8-9]. In related to various chemical compounds, volatile organic compounds (VOCs) also attract much more interest from the last few decades in abundant significant fields like R&D laboratories, industrial productions etc. due to its toxicity, flammability, environmentally hazardousness, and explosiveness [10-11]. So, a rapid detection of VOCs is desired to maintain their concentration within permissible limit and avoid exposure associated health hazards. Chronic exposure of VOCs such as benzene, toluene, ethyl benzene and methanol poses serious health concerns such as skin and sensory irritation, carcinogenesis, mutagenesis, central nervous system depression and respiratory system damage [12-13]. Among VOCs, methanol (MeOH) has been used as an important raw chemicals in various industries as well as household products (drugs, perfumes, colors, dyes, antifreeze, etc) [14]. It is also a valuable alternative automobile fuel as it has already been used for fuel motor vehicles in many countries [14]. On the other hand, methanol has also been strongly injurious to human health as well as environment monitoring due to its toxicity, flammability etc. [15-16]. Inhalation of ~20 mL methanol can lead to blindness, while ~60 mL may cause to fatal accident, if not immediately treated. Hence, early detection of methanol vapor makes a high demand for safety purpose. Though many researchers have developed low power consuming CO_2 as well as methanol sensor with remarkable sensitivity, stability and selectivity [16-19] but, still there is a demand due to high sensitivity, small in size, low cost, and modest operation at room temperature. Even, development of CO_2 sensor operating at room temperature under different humid condition makes another challenge.

Until now, variety of measuring methods have been proposed to measure CO_2 as well as methanol in low concentration level, including optical spectroscopy [9], gas chromatography [20], nondispersive infrared spectroscopy [21], potentiometric and amperometric [22-23], surface and bulk acoustic wave (SWA & BAW) [24], chemiresistive and capacitive-type sensor [25-26]. Among them, chemiresistive type sensor shows high demand due to good sensitivity and stability, smaller in size, low cost, low power consumption and simple operation at room temperature [25,27].

Till date, by following the chemiresistive sensing approach, various kind of inorganic as well as organic materials have been employed in the development of CO_2 as well as methanol (MeOH) sensor, including pure and mixed metal oxide semiconducting materials [28-30], carbon based nanomaterials [26,31-32], polymers and other amine containing polymers [33-35], and polymer based composites [36-37]. However, metal oxide materials are limited by their poor selectivity, high temperature operation, high power consumption, and influence of surrounding parameters [38-39]. On the other hand, polymers and their composites with carbon derivatives have been found to be operated at room temperature and consume low power, but are limited by their sensitivity [34,40]. This limitation could be improved by functionalizing the incorporated carbon based nanofillers or tuning the weight percentage (wt%) of nanofillers inside composite. For example, polymers containing amino groups have been found to be promising sensing materials towards CO_2 gas detection, but small sensing signals in lower concentration makes another challenge [34-35,40]. As reported recently, the sensing signals could be improved by higher concentration of amino group or controlling the amino group in polymer backbone [26].

In addition, polymer nanocomposites having carbon nanotubes (CNTs) or amine functionalized CNTs make a new era in CO_2 gas sensing technology by increasing surface area to volume ratio as well as amine concentration on the surface of the composite [41-43]. The incorporation of CNTs not only improves the gas sensing behaviour but also enhances mechanical strength, electrical properties, thermal and chemical stability of the total composite. In particular, the conductivity of amine based chemiresistive sensor changes due to the formation of carbamates (dry air) and bicarbonates (humid air) upon exposure to the CO_2 gas molecules. For example, Srinives et al. reported a miniature type poly(ethyleneimine) (PEI) functionalized polyaniline (PANI) based nano-thin film chemiresistor, which is able to detect CO_2 gas under different humid condition at room temperature [25]. Alexander et al. developed a carbon nanotubes based field effect transistor (NTFET) by synthesizing PEI and starch polymer where the wireless fabricated sensor could detect CO_2 gas at lower concentration level and able to enhance gas sensitivity in presence of different humidity at ambient temperature [4]. Chang et al. also reported high electron mobility transistors (HEMT) using PEI/starch functionalized materials for CO_2 detection (0.9% to 50%) at higher temperatures (46 - 220 ˚C). Doan and co-workers reported polymer composite based CO_2 sensor by synthesizing sulfonated PANI and polyvinyl alcohol (PVA) where pH dependent conductivity at room temperature under different humidity has been described well [44]. Similarly, by following other sensing methods, various kind of amine containing materials have been used for CO_2 sensing, such as 3-aminopropyltrimethoxysilane [45], PEI and polyallylamine (PAA) [42], isopropylamine, cyclopropylamine and 3-N',N'-dimethylamino propylamine [46], aminoalkylpoly(dimethylsiloxane) (APDMS), poly(propyleneimine) (PPI), and ethylene diamine (EDA) [34]. Apart from the reported research works, it is clear that formation of carbamates and bicarbonates by reversible reaction (HSAB theory) are the primary reason for protonation of amine groups as well as change in total conductivity of the amine-functionalized materials or composite. In principle, primary and secondary amines have greater tendency than tertiary amines to interact CO_2 gas molecules at room temperature by reversible reaction [47]. Similarly, over the last few decades, insulating polymer based composites with different mass fraction of carbon based nanofillers have been influenced as a promising methanol vapor sensing element by making continuous conductance path throughout the composites [48-49]. For example, Lewis et al. developed carbon black (CB)-poly(ethylene-co-vinyl acetate) (PEVA) composite having 25 wt% carbon content and was highly sensitive towards methanol (response time 12 ms) compared to the other VOCs [50]. Morohashi et al. synthesized a sensitive poly(N-isopropylacrylamide) (PNIPAM)-grafted carbon black composite for the detection of methanol vapor at ambient air in addition of 20 wt% carbon black [51]. Iwaki's research group reported a sensor based on carbon black/polyvinylpyrrolidone (PVP) composite film (20 wt% carbon black) to detect methanol vapour in the range of 1360 to 5430 ppm at ambient air [52]. Greenshields and co-workers reported polyvinyl alcohol (PVA)/nitrogen-doped multi-wall carbon nanotubes (N-MWCNTs) composite for the detection of methanol vapor in the detection limit of 410 ppm at ambient air. The as prepared composite was loaded with 0.5 wt% of N-MWCNTs [32]. Wang et al. synthesized poly(4-vinylpyridine) (PVP)/ MWCNTs composite with high sensitivity for methanol vapor at room temperature [53]. Poly(vinyl acetate) (PVAc)/CB (4 wt%) composite was synthesized using surfactants (Hypermer PS3 and Hypermer PS4) by Arshak and co-workers, who reported methanol response in the range 0-12000 ppm at ambient air [54]. Although many efforts have been devoted for developing insulating polymer based methanol sensor by few research groups, the sensor response still suffer from poor sensitivity and repeatability, low signal to noise ratio, and long working temperature range. Furthermore, the sensors with high response to methanol have provoked a great interest in public safety and environmental monitoring.

2. Challenges in the development of polymer composite based carbon dioxide and methanol sensor

Despite of various researches in polymer composite based carbon dioxide and methanol sensor development, there are few important issues which makes challenge in their sensing precise measurement. These issues are described below:

a) CO_2 detection in surrounding environment has continued to be a great challenge due to inertness and presence of other interfering species, like nitrogen dioxide (NO_2) and carbon monoxide (CO) etc.

b) Development of CO_2 sensor operating at room temperature under different humid condition.

c) Though, polymers containing amino groups have been found to be promising sensing materials towards CO_2 gas detection, but small sensing signals in lower concentration makes another challenge.

d) Even, agglomeration of carbon based nanofillers inside composite makes a serious issue.

e) In case of methanol sensing, sensor response still suffer from poor sensitivity, repeatability, low signal to noise ratio, and long working temperature range.

3. Research Gaps

Though, various researches haven carried out in CO_2 as well as methanol sensing to improve sensor sensitivity at room temperature under different humid condition, still the reported sensor suffer from poor sensitivity and repeatability, low signal to noise ratio, and long working temperature range, different humid condition etc. These important issues are highlighted with reported research work as follows.

a) Over the last few decades, insulating polymer based composites with different mass fraction of carbon based nanofillers have been influenced as a promising methanol (MeOH) vapor sensing element by making continuous conductance path throughout the composites [48-49]. To enhance the sensitivity, many researchers tried to incorporate higher percentage (%) of carbon based nanofillers like carbon black (CB), Carbon nanotubes (CNTs), graphene oxide (GO), and reduced graphene oxide (rGO) [32,50,53]. But, agglomeration of nanofillers due to higher concentration level makes it difficult for uniform gas adsorption throughout the composite and hence the sensor sensitivity. Moreover, higher concentration makes the fabricated sensor cost high.

b) Though, polymers are good candidate for methanol sensing, but they are lacking from high sensitivity. Many conducting and insulating polymers like poly(ethylene-co-vinyl acetate) (PEVA), poly(N-isopropylacrylamide) (PNIPAM), polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), Polyaniline (PANI) etc. and their composites have been used for methanol sensing [32, 50-53]. But, it could be a good strategy by making the polar composite for more attraction of methanol molecules on sensor surface. In this regards, insulating poly(etherimide) (PEI) and semi-crystalline of liquid crystal polymer (LCP) as a vapor sensing material because of its low cost and good chemical as well as thermal stability [55-56]. Incorporation nanofillers like CB, CNTs, and rGO could enhance the sensor sensitivity. Moreover, sulfonation of the polymer composite could make the senor more polar.

c) On the other hand, polymers and their composites with carbon derivatives have been found to be good material for CO_2 sensing which operated at room temperature and consume low power, but are limited by their sensitivity [34,40]. In this regards, polymers containing amino groups could be a promising sensing materials towards CO_2 gas detection. Though, many researches have been reported using poly(ethyleneimine) (PEI) [4,25,57] but, presence of tertiary amines do not involve any interaction with CO_2 gas molecules. So, it may be a good strategy to use primary and secondary amines as CO_2 sensing material which have greater tendency than tertiary amines to interact CO_2 gas molecules at room temperature by reversible reaction [47]. In this regard, primary amine like ethylenediamine (EDA) and secondary amine like diethanolamine (DEA) could play vital role in CO_2 gas detection.

d) Presence of humidity in our surrounding environment is another important issue for CO_2 detection. Many researchers have also tried to sense CO_2 gas in presence of different humidity [4,25,44]. Still now, it is a great challenge for getting large sensitivity towards CO_2 gas in presence of humidity. But, presence of humidity could be used in favor of acidic CO_2 gas sensing. It has been reported that sulfonation of polymer helps to attract much more water molecules from humid environment, which generate bicarbonate ions (HCO_3^-) by following Hard Soft Acid Base (HSAB) theory. Hence, enhance the sensor sensitivity by increasing sensor conductivity. For example, sulfonated PANI and polyvinyl alcohol (PVA) has been used for better sensitivity towards CO_2 gas [44]. But, very few researches have been reported by using sulfonation of the polymer. In this regards, sulfonated polyethersulfone (SPES) and sulfonated poly (ether ether ketone) (SPEEK) could be good candidate for their CO_2 adsorption capability [58-60]. Also, degree of sulfonation of polymer increases the CO_2 gas permeability throughout the polymer composite based chemiresistive sensor.

e) In addition, polymer nanocomposites having carbon nanotubes (CNTs) or amine functionalized CNTs make a new era in CO_2 gas sensing technology by increasing surface area to volume ratio as well as amine concentration on the surface of the composite [26-28]. But, small sensing signal in amine functionalized material makes another difficulty to get high sensitivity towards CO_2 gas. It could be improved by tuning the amine concentration into functionalized CNTs. So, it will be a good strategy to make polymer composite based chemiresistive sensor using ethylenediamine (EDA) and diethanolamine (DEA) funtionalized MWCNTs incorporated in sulfonated polyethersulfone (SPES) and sulfonated poly (ether ether ketone) (SPEEK) matrix separately.

4. Main objectives of thesis work

a) Fabrication of carbon nanofillers based thin film chemiresistive sensor for toxic gas detection like CO_2 and methanol at low concentration level.

b) Gas sensing measurement under different ambient conditions.

c) Improvement in sensitivity towards methanol and CO_2 gas at low concentration level.

d) Repeatability and selectivity test of the target gas.

5. Material and Methods

5.1 Material and Chemicals

References Poly(etherimide) (PEI) AUT 200, (Sabic Innovative India Ltd., India), and liquid crystal polymer (LCP) LCPG30-02BK, (Next Polymers Ltd., India), were used to prepare the base composite material. Sulfuric acid (H_2SO_4) (Himedia, 98.0 wt %) was used to dissolve polymers as well as for sulfonation of the composites. Methanol (MeOH) (Avantor, 99.0%) analyte was utilized as a target analyte. Hydrochloric acid, HCL (Himedia, 35%), Nitric acid, HNO_3 (Avantor, 72%), Potassium permanganate, $KMnO_4$ (Avantor, 99.0%), Hydrogen peroxide, H_2O_2 (Avantor, 30.0%), Sodium borohydride, $NaBH_4$, (Avantor, 98.0%) were used to prepare reduced graphene oxide form graphite powders, (S. K. Carbon Ltd., 98.5%, India). Carbon black (CB) PC503, (Philips Carbon Black Ltd., India), multi-wall carbon nanotubes (MWCNT), (Hanwha Nanotech Co., Republic of Korea), Reduced graphene oxide (RGO) (prepared in our advanced composite laboratory, IIT Roorkee) were utilized as conductive nanofillers. For all cases double distilled water was used whenever required. Ethylenediamine (EDA) (Sisco, 99%) was used for functionalization of multi-wall carbon nanotubes (MWCNTs). thionyl chloride

(SOCl2) (Transpek, 98%), Dimethylformamide (DMF) (Himedia, 99.5%), tetrahydrofuran (THF) (Avantor, 99.5%), and ethanol (Changshu Hongsheng, 99.9%) were used for EDA functionalization of MWCNTs as well as preparation of composites. Diethanolamine (DEA) (Sisco, 99%) was used for MWCNTs functionalization. The semi-crystalline matrix poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) (Sigma-Aldrich Co. Ltd., UK) with Mn =10300, Mw = 20800, relative density 1.3 g mL-1 at 25 ˚C, and melting point at 322 ˚C was used to prepare sulfonated PEEK (SPEEK) with different DS as well as composites. In every synthesizing process deionized water (DI water) was used as per requirement. In every synthesizing process deionized water (DI water) was used as per requirement.

5.2 Characterization Techniques

The chemical structure of the investigated materials was characterized by Thermo-Nicolet Fourier transform infrared spectrometer (FT-IR). The surface morphology and microstructure of the prepared sensing films were examined by FEI Quanta 200 F field emission scanning electronic microscopy (FESEM) at an accelerating voltage 15 kV. The elemental analysis of the composite films was recorded by energy dispersive x-ray (EDX) linked with FESEM. The crystallinity analysis was performed by a Bruker AXS D8 Advance powder X-ray diffractometer (XRD) with Cu-Kα radiation source (1.5418 Å). The current-voltage relationship of the fabricated sensors was obtained using two probe method (Zahner (PP211) with a DC bias voltage from -4 to +4 V. The surface topographies as well as thickness measurement of the sensing films were investigated by NTEGRA atomic force microscopy (AFM).

5.3 Sensor fabrication and Experimental setup

The glass slides (7.5 × 2.5 cm^2) with a thickness of 1.2 mm were cut into a size of 2.5 × 0.5 cm^2 strips followed by well-cleaning process using piranha solution (3:1 mixture of H_2SO_4 with H_2O_2) to remove any organic residues from the surface of the substrate. Two copper plates as electrode (with a dimension of 20 mm × 4.65 mm × 0.16 mm) were exquisitely equipped at the two ends of each strip with conductive silver paste, leaving a gap of 5 × 5 mm^2 for vapor sensing test. For electrical connectivity between sensor and controlled DC power supply, a 10 cm long copper wire (having 0.6 mm diameter) was soldered at each end of the electrodes. The open areas of the electrodes were wrapped by teflon tape to avoid any chemical reaction from target analyte or any other surrounding substances. In thin film sensor fabrication, the prepared sPEI-LCP, sPEI-LCP/CB, sPEI-LCP/MWCNT, and sPEI-LCP/RGO composite solutions were deposited distinctly on empty area (gap between electrodes) of the decorated strips by drop casting method followed by drying in air conditioning room for one week. The schematic for sensor fabrication process is presented in Fig. 1. Methanol sensing measurements was carried out by homemade sensing setup as shown in Fig. 2.

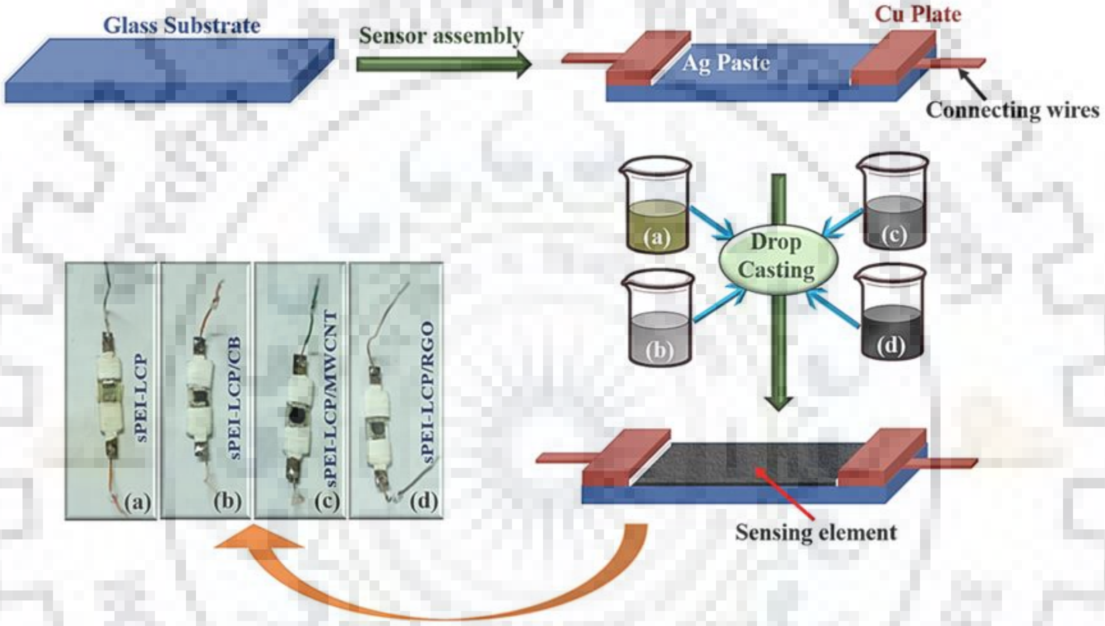

Fig. 1. The schematic for sensor fabrication process with prepared chemiresistive type fabricated sensors based on (a) sPEI-LCP (b) sPEI-LCP/CB (c) sPEI-LCP/MWCNT (d) sPEI-LCP/RGO composite.

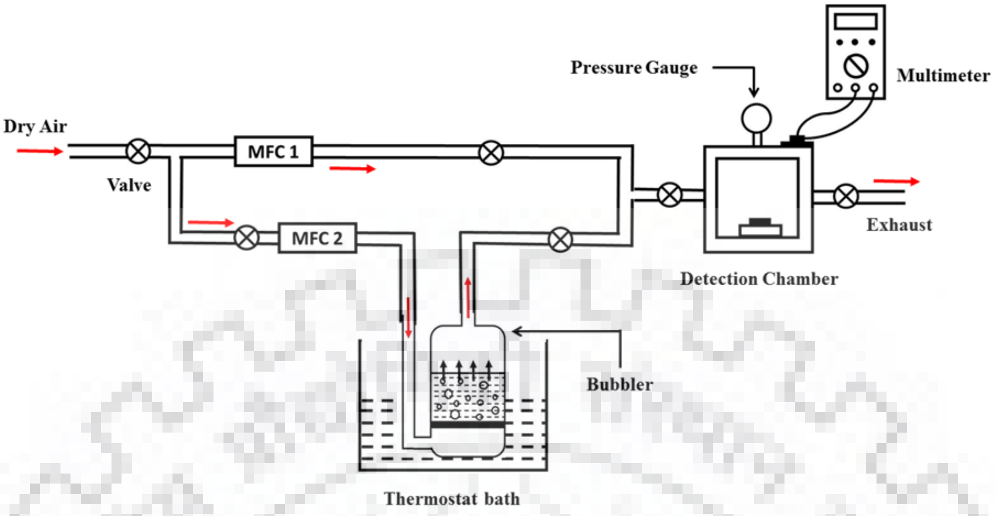

Fig. 2. Schematic diagram of methanol sensing measurement system.

For the detection of CO_2 gas sensing, the as prepared composites (SPEEK-1/d-MWCNTs, SPEEK-2/d-MWCNTs, SPEEK-3/d-MWCNTs, SPEEK-4/d-MWCNTs, and SPEEK-5/d-MWCNTs) were drop casted distinctly on the leaving area of the decorated strips followed by the vacuum dry at room temperature (27 ˚C) for 2 days. The schematic for sensor fabrication technique is presented in Fig. 3.

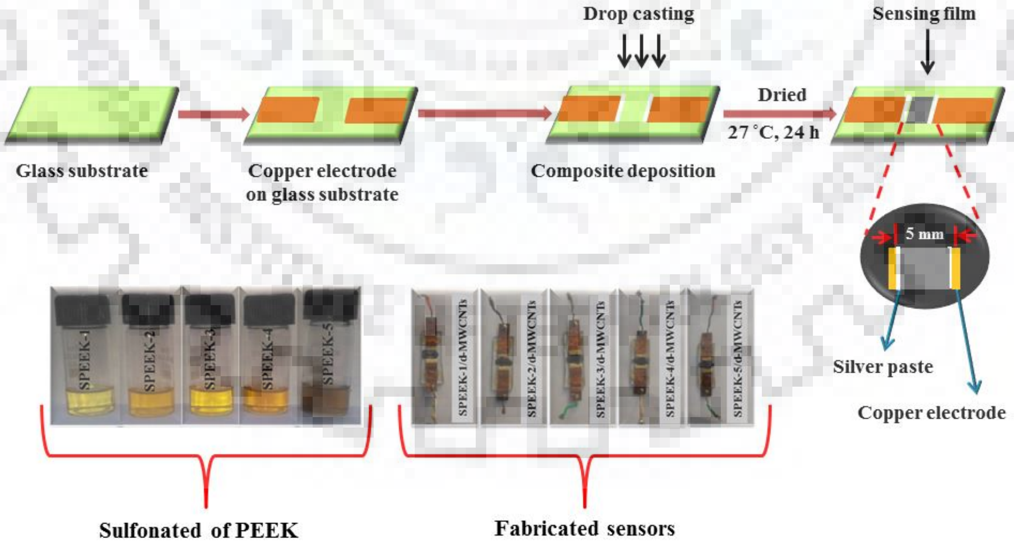

Fig. 3. Schematic of fabrication technique to prepare chemiresitive sensor based on (a) SPEEK-1/d-MWCNTs (b) SPEEK-2/d-MWCNTs (c) SPEEK-3/d-MWCNTs (d) SPEEK-4/d-MWCNTs (e) SPEEK-5/d-MWCNTs.

Another film fabrication technique was also applied for CO_2 gas detection where a PCB (10 x 5 cm^2) having thickness of 1.6 mm was cut into a size of 3 × 1 cm^2 strips and were designed with 5 × 5 mm^2 gap on each of the strip for gas sensing test followed by acid etching process using Ferric Chloride ($FeCl_3$). A copper wire with 0.6 mm diameter was soldered at each end of the designed strip for electrical connection between fabricated sensor and regulated DC power supply. In sensor fabrication, 1 μL of PES/e-MWCNTs and SPES/e-MWCNTs composite solutions with different volumetric ratios were drop casted separately in the empty area (5 × 5 mm^2 gap) of the designed PCB strips. The drop casted PCB strips were vacuum-dried at room temperature (27 ˚C) for 24 h. Thus, PES/e-MWCNTs and SPES/e-MWCNTs composite based thin film sensors were prepared with different volumetric ratios of 1:1, 1:2, 1:3, 1:4. The schematic for sensor fabrication process is presented in Fig. 4.

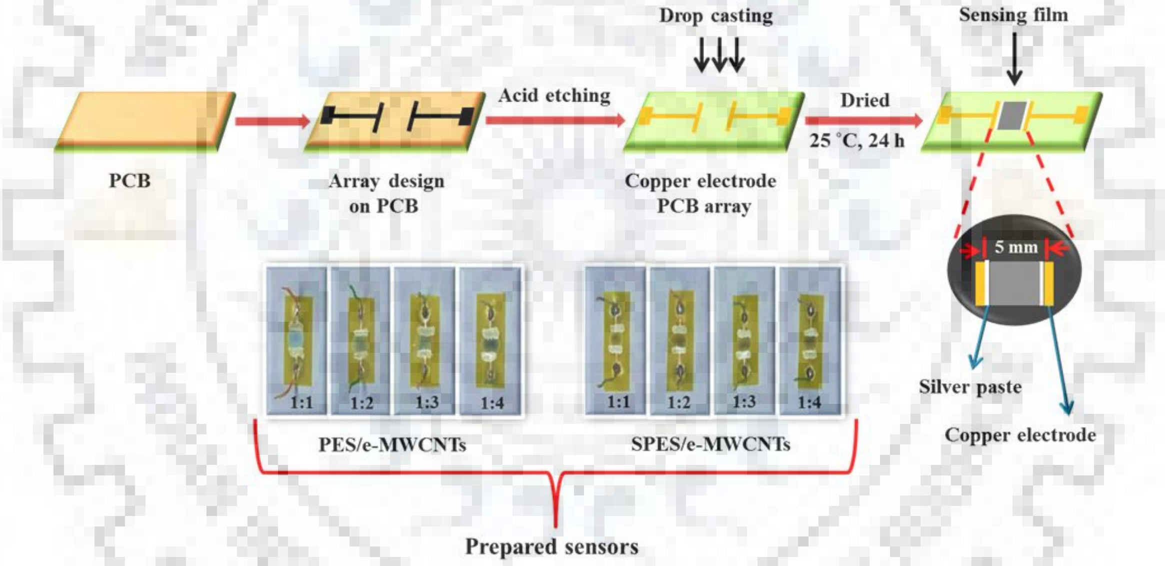

Fig. 4. Schematic of PCB based CO_2 gas sensor fabrication process for PES/e-MWCNTs and SPES/e-MWCNTs composite.

A homemade setup was made to carry out the gas sensing studies as schematically shown in Fig. 5, where a known volume of test chamber was assembled with two mass flow controllers (MFCs; 5850E, Brooks Instrument), a liquid flow meter (LFM), and a controlled evaporator mixer (CEM; Bronkhorst, The Netherlands) for controlling the dry air flow as well as desired

CO_2 concentration and humidified air inside test chamber. A hygrometer (Neoteck, India) was also equipped to the test camber for monitoring humidity (with accuracy ±2% RH) as well as temperature (with accuracy ±0.2 ˚C) during the entire experiment. A rotary connector was fitted on the top of test chamber for electrical connection purpose.

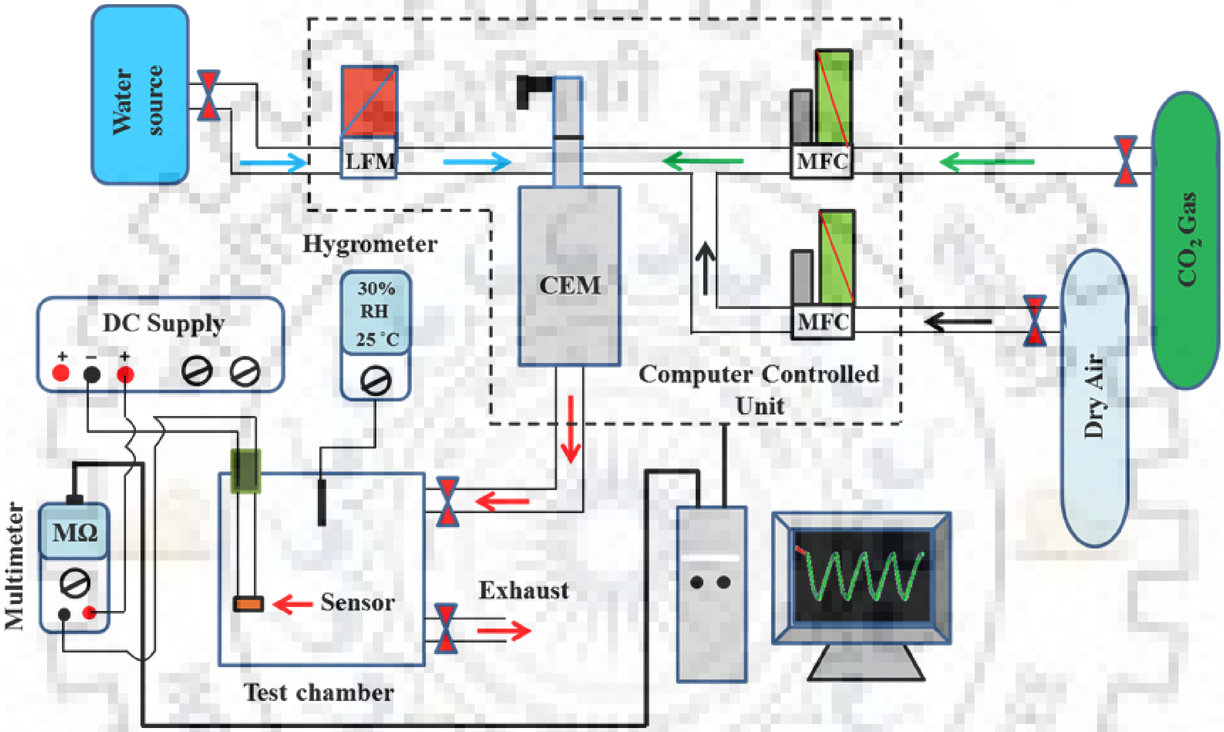

Fig. 5. Schematic representation of homemade CO_2 gas sensing setup

6. Main observation from the obtained results

- The incorporation of nanofiller induces the dramatic change in sensing behavior of base composite film (sPEI-LCP). Thus, less mass fraction of nanofillers (i.e. 2 wt%) influence the sensing behavior of sulfonated PEI-LCP/CB (sPEI-LCP/CB), sulfonated PEI-LCP/MWCNTs (sPEI-LCP/MWCNTs), and sulfonated PEI-LCP/RGO (sPEI-LCP/RGO) based composite for the entire range (300 – 1200 ppm) of methanol vapor.

- Among other chemiresistive fabricated sensors (sPEI-LCP/CB and sPEI-LCP/MWCNT), sPEI-LCP/RGO based sensor shows the highest dynamic sensing response for the entire range of methanol concentration (300 – 1200 ppm) and having a sequential values as follows 14.47%, 31.02%, 53.1%, and 92%, respectively.

- The repeatability has been measured at 300 ppm methanol vapor concentration for four consecutive cycle (90 s). The obtained results reveal that, all the prepared sensors have been affected insignificantly by the surrounding environment.

- A selectivity test has been conducted for all the prepared sensors towards some common volatile organic compounds, such as ethanol, 1-propanol, 2-propanol, and n-butanol (all of them were 600 ppm) at room temperature. The obtained results show that all the sensors are more sensitive toward methanol compared to other examined analytes.

- Chemiresistive type carbon dioxide (CO_2) gas sensors using different degree of sulfonated poly (ether ether ketone) (SPEEK) incorporated with diethanolamine (DEA)-functionalized multi-wall carbon nanotubes (d-MWCNTs) have been developed. In sensing properties, SPEEK-5/d-MWCNTs (degree of sulfonation, i.e., DS = 71.03%) based sensor shows highest sensitivities (3.98×10^{-3} – 7.83×10^{-3} % ppm^{-1}) for the entire gas sensing measurement (500 - 5000 ppm) under different relative humidity (30 - 70% RH) at room temperature.

- The interaction mechanism mainly depends on the charge transportation between CO_2 gas molecules and amine functionalized MWCNTs (d-MWCNTs). In addition, formation of bicarbonate ions (HCO_3^-) during interaction enhances the sensor sensitivity in presence of different relative humidity

- The repeatability test of the SPEEK-5/d-MWCNTs based sensor has been executed towards 2000 ppm of CO_2 gas at 30% RH for four consecutive cycles. SPEEK-5/d-MWCNTs based sensor showed good repeatability among other fabricated sensors.
- In selectivity measurements, SPEEK-5/d-MWCNTs based sensor was tested against some common toxic gases (5 ppm NO_2 and 50 ppm NH_3) and organic vapors (200 ppm methanol (CH_3OH), 1000 ppm ethanol (C_2H_5OH), and 500 ppm acetone (C_3H_6O)) at 30% RH. The obtained result shows that prepared sensor is more selective towrds CO_2 gas compared to other gases.
- The limit of detection (LOD) was determined as 3 times standard deviation of the blank sample (sensor response in humidified air only) divided by slope of linear part of the calibration curve. In comparison, SPEEK-5/d-MWCNTs based sensor shows the lowest LOD (32 ppm) for the entire CO_2 gas concentration at 70% RH.
- Chemiresistive type Carbon dioxide (CO_2) gas sensors using polyethersulfone (PES) and sulfonated PES (SPES) incorporated with ethylenediamine (EDA)-functionalized multi-wall carbon nanotubes (e-MWCNTs) have been developed. In sensing properties, SPES/e-MWCNTs based sensor showed highest sensitivities (4.94×10^{-3} – 6.49×10^{-3} % ppm^{-1}) as compared to the PES/e-MWCNTs (2.1×10^{-3} – 2.94×10^{-3} % ppm^{-1}) based sensor for the entire gas sensing measurement (500 - 5000 ppm) under different relative humidity (30 - 70% RH) at room temperature.
- In case of SPES/e-MWCNTs based sensor, LODs were found to be about 50, 42, and 35 ppm for the entire CO_2 gas concentration at 30%, 50%, and 70% RH, respectively.
- In repeatability test, PES/e-MWCNTs and SPES/e-MWCNTs based sensor shows very negligible drift which means sensors have been affected insignificantly by local environment.

- In selectivity test, SPES/e-MWCNTs based sensor shows more selectivity towrds CO_2 gas than other toxic gases.
- Finally, this work assists the development of cost effective polymer composite based chemiresistive methanol and CO_2 gas sensor operating under different ambient condition.

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List of Publications from Present Work

1. **S. Bag**, K. Rathi, and K. Pal, *"Effect of carbon derivatives in sulfonated poly(etherimide)–liquid crystal polymer composite for methanol vapor sensing"*, ***Nanotechnology*** 28 (2017) 205501. [I.F.: 3.40]

2. **S. Bag**, and K. Pal, *"A PCB based chemiresistive carbon dioxide sensor operating at room temperature under different relative humidity"*, (***IEEE Transactions on Nanotechnology***, Under Review).

3. **S. Bag**, and K. Pal, *"Sulfonated poly (ether ether ketone) based carbon dioxide gas sensor: Impact of sulfonation degree on sensing behavior at different humid condition"*, (***Sensors and Actuators B: Chemical***, Just Accepted). [I.F.: 6.393]

List of Publications other than Present Work

1. K. Pal, V. Panwar, **S. Bag**, J. Manuel, J.H. Ahn, and J.K. Kim, *"Graphene oxide–polyaniline–polypyrrole nanocomposite for a supercapacitor electrode"*, **RSC Adv.** 5 (2015) 3005-3010.

2. N. Debnath, V. Panwar, **S. Bag**, M. Saha, and K. Pal, *"Effect of carbon black and nanoclay on mechanical and thermal properties of ABS–PANI/ABS–PPy blends"*, **J. APPL. POLYM. SCI.** 132 (2015) 42577.

International Conferences

1. **S. Bag**, and K. Pal, *"A PCB based chemiresistive carbon dioxide sensor operating at room temperature under different relative humidity"*, **2018 IEEE 13th Nanotechnology Materials and Devices Conference (NMDC)**, DOI: 10.1109/NMDC.2018.8605852.

2. **S. Bag**, and K. Pal, *"A novel sensor for detection of methanol vapor based on conductive amorphous polymer composite: multi-wall carbon nanotubes/poly(etherimide)"*, **3rd International Conference on Nanotechnology for Better Living (ICNBL-2016)**, DOI: 10.3850/978-981-09-7519-7nbl16-rps-187.