Strontium arsename doped conducting polyaniline matrix as gas sensor

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Abstract. Electrical response of strontium arsename (Sr3(AsO4)2) doped conducting Polyaniline (PANI) composites matrix in liquid petroleum gas (LPG) environment is studied. One step in situ chemical polymerization technique was used to synthesis conducting PANI and PANI / Sr3(AsO4)2 composites. Characterization confirmed the formation conducting polymer by FTIR, presence of Sr3(AsO4)2 in PANI matrix and its crystallinity by X-RD, Surface morphology and porosity by ESEM. Conductivity increases by with temperature, due to ion transfer within the composites by curling behavior of polymer. Absorption of charges by analyte gas from polymer matrix due to electron affinity, increases electrical resistance with increase in concentration of LPG. The absorption of the charges depends on the surface area of interaction between analyte gas and polymer matrix.

1. Introduction
Metal oxide semiconducting gas sensors with good electrical properties are available, operable at high temperature that consumes more power. To overcome this problem and ensure improved sensitivity and selectivity, dissimilar methods have been explored in the past few years. In search of effective gas sensing materials researchers have opted conducting polymers and polymer / metal oxide composites. Considerable research work has been reported on conducting polymer composites for gas sensing behavior and mechanism involved using various combinations of metal oxides [1-6]. Possibly perilous gases which are burnable like residential fluid oil gas (LPG) and carbon monoxide (CO) causes ignition mishaps by spillage or misstep. Much of the attention has been focused to prevent the combustion accidents by the study of hazardous gas sensors [7-8]. Sensor is determined as a device converting chemical information into an electrical signal in different concentrations of chemical environment or gas species. The physical properties of different materials have been altered after the interaction of chemical environments, such materials are metals, ionic mixes (metal oxides and bimetal oxides), polymers and excessively sub-atomic structures [9]. Modern and residential reason, hydrocarbon gases are utilized as fuel, it is verifiable truth that the utilization of melted oil gas (LPG) expanded, additionally expanded the event of incidental blasts because of spillage. Hence, it is required for the improvement of reliable and touchy gas identifying gadgets/instruments to expand the security at home and industry. The constituents of LPG are propylene (C3H6), propane (C3H8), butylene (C4H8) and butane (C4H10). The business quality items promoted as butane and propane, not
unadulterated synthetic hydrocarbons but rather additionally contain follow characteristics of other comparable gases. The exploration has been centered around propane or butane gas sensors, yet little work has been accounted for on LPG sensors. Writing overview delights that, by and by accessible sensors have two significant lacks, activity at high temperature and low affectability, however one needs to settle on any of these characteristics. A high touchy sensor that works at high working temperature devours more force, on opposite side the sensors that works at low-temperature has low affectability, which isn't sufficient for the recognition of follow level LPG [10-14]. Polyaniline / molybdenum oxide (MoO$_3$) composites are studied for LPG sensing, found to have high sensitivity for the composites of 10, 40 and 50 wt% of MoO$_3$ in PANI and selectivity after exposing to LPG, ethanol, H$_2$S gas and oxyacetylene were reported. The maximum sensitivity of 78 % and 80 % is reported for LPG with 10 and 50 wt% of MoO$_3$ in PANI respectively, also response time has been appraised to be 11.66 and 13.33 minutes for LPG [15]. Cadmium oxide (CdO) / PANI composites have shown good sensitivity and selectivity due to the use of nanoscaled PANI grains, so that maximum surface area of CdO was exposed to the gas to improve the sensing mechanism. These sensors using CdO/PANI composites for LPG detection has two advantages, operating temperature comes down from 700 °C to room temperature which increases the life of sensor element and interacting gases are less active when compared to LPG. These sensor shown good selectivity for LPG, the sensing response of CdO/PANI was recorded for as minimum as concentration of LPG was 200 ppm. The selectivity of CdO/PANI is found to be maximum for LPG and moderate for ethanol. The high sensitivity of CdO/PANI composites is about 75% for LPG at 400 ppm was recorded [16]. Polyaniline / CeO$_2$ composite in which N-type CeO$_2$/P-type polyaniline have formed a hetero-junctions and distributed in bulk throughout the sample. PANI / CeO$_2$ composite were studied by exposing to LPG, on absorption of gas by emeraldine based polyaniline, it reacts with imine Nitrogen atom to produce protonated form of polyaniline affecting significant changes in conductivity. The presence of CeO$_2$ in PANI helps to stimulate this reaction. It was observed that in all PANI / CeO$_2$ composites, as gas concentrations increases resistance also increases. The maximum sensitivity was recorded for 20 wt% CeO$_2$ in PANI [17]. The adjustment in opposition of PANI/BaZrO$_3$ composites was recorded with time by expanding LPG fixation reliably. It is seen that with increment in gas focus the opposition of the composites likewise increments. Most extreme change in obstruction is found in composites of 40 and 50 wt% BaZrO$_3$ in PANI when contrasted with different composites and unadulterated PANI. The component of detecting in these composites is because of the decline in electronic conduction by adsorbed oxygen on the outside of BaZrO$_3$. An electron is assimilated from the conduction band of BaZrO$_3$ by barometrical oxygen atoms and go about as contributor. When diminishing gas particle responds negative oxygen molecule and give back the electron caught to conduction band, henceforth the conductivity of the sensor increments. Affectability of polyaniline and PANI/BaZrO$_3$ composites were accounted for out which most extreme affectability is seen in composite of 50 wt% of BaZrO$_3$ in PANI is promising materials for LPG sensor [18]. Properties of the detecting materials, for example, atomic size, extremity, polarizability, proclivity, alongside coordinating qualities administers the cooperation of test gas and detecting material. In the present study a combination of organic and inorganic materials composites are selected to develop sensing material for gas sensors. In our study polyaniline (PANI) as organic material and inorganic Strontium arsenate (Sr$_3$(AsO$_4$)$_2$).

2. Experimental
PANI / Sr$_3$(AsO$_4$)$_2$ composite matrix of weight percentages (10, 20, 30, 40, 50) has been synthesized by single step chemical (in-situ) polymerization technique with an oxidizing agent ammonium persulphate [(NH$_4$)$_2$S$_2$O$_8$] at a temperature of 0 to 5°C in freezing mixture with rigorous stirring. The obtained dark green precipitate of composites are washed with deionized water and dried in oven for 24 hours. The dry powder of composites are pressed to form pellets of 10 mm diameter and thickness 1.5 mm by applying hydraulic pressure of 10 ton using Universal Testing Machine (UTM-40). The pellets formed from polymer matrix composite powder are provided with silver pasted electrodes for the study of electrical response. Perkin – Elmer 1600 spectrometer is used to record Fourier Transform Infrared (FTIR) spectra of polymer composite in KBr medium. Phillips X – ray diffractometer
(PW3710) is used to record X-ray diffraction (X-RD) pattern of polymer matrix with Cu Kα radiation source. Phillips XL 30 ESEM scanning electron microscope is used to record the images of polymer matrix to investigate the surface morphology of the composites. [19]. The temperature dependent conductivity has been measured as variation of planar resistance by varying temperature using Keithely - 2000 multimeter (USA) with temperature controlled oven. The closed gas sensor chamber of glass is used to study gas sensor behavior of polymer composite. LPG is allowed to enter the sensor chamber through flow meter at the rate of 25 ml/min by regulating the flow from the cylinder. The change in planar resistance of conducting polymer matrix were recorded at regular interval of 20 seconds, such that the gas concentration is 0.42 ml / sec with a concentration of 8.33 ml for every recording.

3. Results & discussions

3.1 FTIR Spectroscopy
‘Figure 1’ shows FTIR Spectra of PANI/Sr$_3$(AsO$_4$)$_2$ (50 wt %) composite. Presence of metal - oxygen bond is confirmed by the stretching frequencies in the spectra with peaks 796 cm$^{-1}$ and 508 cm$^{-1}$, which shows presence of Sr$_3$(AsO$_4$)$_2$ in polymer matrix. Formation of conducting polymer is confirmed from other spectral peaks and their structural bond assignments as follows. N-H bond stretching at peak of 3435 cm$^{-1}$, ring structure of polyaniline is at peak 1568 cm$^{-1}$, C=N bond stretching & C-C bond stretching are at peak 1483 cm$^{-1}$, C-N bond stretching with C-H bond bending are at peak 1294 cm$^{-1}$ for, C-N bond stretching with C-C bond stretching at peak 1240 cm$^{-1}$. The metal-oxygen stretching frequencies have been shifted from 800 cm$^{-1}$ and 705 cm$^{-1}$ of pure Sr$_3$(AsO$_4$)$_2$ to 796 cm$^{-1}$ and 508 cm$^{-1}$ of Sr$_3$(AsO$_4$)$_2$ - polymer matrix. This observation confirms that, the Vander walls kind of interaction between PANI chain and Sr$_3$(AsO$_4$)$_2$, because the metal-oxygen frequencies are shifted towards higher side of the spectra in the formation of polymer composite [20-23].

3.2 X – Ray Diffraction
‘Figure (2)’ shows the X-ray diffraction pattern of composite with 50 wt % of Sr$_3$ (AsO$_4$)$_2$ in PANI. The Rhombohedral peak of Sr$_3$(AsO$_4$)$_2$ indicated in X-ray diffraction pattern of JCPDS 13 – 0261 of Sr$_3$(AsO$_4$)$_2$ is confirmed from the X-ray diffraction studies of the PANI - Sr$_3$(AsO$_4$)$_2$ composite. The prominent peaks corresponding to 2θ = 32.11°, 38.62°, 42.88°, 56.72° and 68.36° are due to the crystal planes of (110), (202), (024), (300) and (220) in consistence with the X-ray diffraction studies of pure Sr$_3$(AsO$_4$)$_2$. This study confirms that the crystalline structure of Strontium arsenate has been retained even though it is doped in PANI during polymerization. [24]

![Figure 1. FTIR of PANI / Sr$_3$(AsO$_4$)$_2$ composite.](image1)

![Figure 2. X-RD of PANI/Sr$_3$(AsO$_4$)$_2$ composite.](image2)
3.3 Scanning electron microscopy

‘Figure 3 (a)’ Shows ESEM image of pure PANI, ‘Figure 3 (b)’ Shows ESEM image of PANI / Sr$_3$(AsO$_4$)$_2$ composite with 50 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI. The ESEM image of pure PANI indicates chain / branched morphology with porous structure. The ESEM image of PANI/Sr$_3$(AsO$_4$)$_2$ composite shows chain / branched morphology along with distribution of crystalline Sr$_3$(AsO$_4$)$_2$ throughout PANI matrix homogeneously. The ESEM image of the composite (b) shows branched porous structure and presence of capillary pores inter connected with each other, which facilitate large surface area of interaction for analyte gas to penetrate through the composite for better sensing activity.

3.4 dc – Conductivity

‘Figure (4)’ shows the temperature dependent conductivity of PANI and PANI / Sr$_3$(AsO$_4$)$_2$ composite. It was observed that the conductivity increases with increase in temperature indicates thermally activated behavior of conducting polymers. It is suggested that, thermal curling effect is responsible for increase in conductivity due to increase in conjugate length of the polymer.

![Figure 3 (a). SEM of Pure PANI](image)

![Figure 3 (b). SEM of PANI / Sr$_3$(AsO$_4$)$_2$ composite.](image)

![Figure 4 (a). Variation of $\sigma_{dc}$ as a function of temperature of pure PANI.](image)

![Figure 4 (b). Variation of $\sigma_{dc}$ as a function of temperature of PANI / Sr$_3$(AsO$_4$)$_2$ composites.](image)
Increase in conjugate length indicates the change in molecular arrangement, this will favor electron delocalization responsible for increase in conductivity. Mott proposed variable range hopping (VRH) model to explain the theory of conductivity in conducting polymers [25-27].

3.5 Gas sensing (LPG)

‘Figure 5’ shows the change in resistance as function of gas concentration for pure PANI, ‘Figure 6’ shows the variation of change in resistance as function of gas concentration of PANI / Sr₃(AsO₄)₂ composites. The change in electrical resistance may be either increase or decrease, that depends on type of dopants used in PANI, such as bimetal oxides (ceramics), metal oxides, biomaterials, etc. The transfer of charges from composites to analyte gas will increase the resistance and transfer of charges from analyte gas to composite will decrease the resistance. In case of pure PANI, the sensing mechanism is due to penetration of test gas followed by swelling of polymer. The sensing mechanism in pure Sr₃(AsO₄)₂ is due to surface charge transfer through atmospheric oxygen and/or transfer the charge of interstitial lattice oxygen. In PANI / Sr₃(AsO₄)₂ composite the sensing mechanism is both due to swelling of polymer and surface charge transfer through atmosphere and/or interstitial lattice oxygen. The sensing response of these polymer composites is much high when compared to polymer and ceramic sensing [28].

The gas-detecting system is clarified as far as variety of opposition and subsequently conductivity of detecting material. The variety of opposition is by adsorption of air oxygen on the detecting surface, cross section oxygen or interstitial oxygen response with the detecting material. In the principal case, an electron is separated from the detecting material by climatic oxygen adsorption on a superficial level by decreasing the conductivity. This marvel is principally liable for the discovery of the gases by detecting material. In the subsequent case, the cross section oxygen or interstitial oxygen present in detecting material will associate with test gas and move the charge to test gas. These are the foundations for diminishing conductivity and increments in obstruction of the detecting material within the sight of the test gas [16, 29].

Figure 5. Change in resistance as a function of gas concentration of pure PANI.

Figure 6. Change in resistance as a function of gas concentration of PANI / Sr₃(AsO₄)₂.
Davis S. R et al., proposed the Per-detecting system for metal oxides. Per-detecting component is the arrangement of charge surface upon metal oxide spaces and charge move from detecting material to test gas. This instrument builds the opposition of the detecting material again this expansion will rely upon the particular surface zone of the detecting material that is presented to gas condition [30-31].

The change in resistance of PANI / Sr$_3$(AsO$_4$)$_2$ composite is 180 times more than pure PANI, this confirms surface area interaction is more in composites, doping of Sr$_3$(AsO$_4$)$_2$ has increased the porosity of the composite as revealed by ESEM. It is observed that for 20 & 30 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI change in resistance increases, this results shows that analyte gas has large surface of interaction due to formation of large charge surface and presence interstitial oxygen atoms. While 10 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI shows very low change in resistance, it is much lower than the pure PANI, this may be due to low porosity and small surface area of interaction, this composite is same as pure PANI because of low concentration Sr$_3$(AsO$_4$)$_2$. For 40 & 50 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI shows low change in resistance due to high concentration Sr$_3$(AsO$_4$)$_2$, which reduces interstitial oxygen atoms and forms small charge surface over the composite. [30]

| Composite          | Resistance at gas concentration (LPG) (In Ohms) | Range of resistance change (In Ohms) |
|--------------------|-----------------------------------------------|-------------------------------------|
| PANI               | 0.3                                          | 83.7                                |
| PANI / 10 wt% Sr$_3$(AsO$_4$)$_2$ | 3                                             | 60                                 |
| PANI / 20 wt% Sr$_3$(AsO$_4$)$_2$     | 54                                            | 1544                                |
| PANI / 30 wt% Sr$_3$(AsO$_4$)$_2$     | 16                                            | 1077                                |
| PANI / 40 wt% Sr$_3$(AsO$_4$)$_2$     | 83                                            | 753                                 |
| PANI / 50 wt% Sr$_3$(AsO$_4$)$_2$     | 43                                            | 729                                 |

‘Table 1’ gives the resistance of the composites at initial gas concentration of 925 PPMV and final gas concentration of 22,264 PPMV is given in Ohms, range of resistance change from initial to final is also given. This data is very much useful in the design of sensor device, because sensor is the one which convert the change in environment to an electrical signal. The range of change in resistance is more in PANI / 20 wt% Sr$_3$(AsO$_4$)$_2$ of the order of 1.49 kΩ and PANI / 30 wt% Sr$_3$(AsO$_4$)$_2$ of the order of 1.061 kΩ, this shows that these composites has a huge range of change which is sufficient to change the electrical parameters when used in circuit. These two composites can also be synthesized in the form of thin film so that resolution of resistance increaces with size. This data clearly shows that these two composites are promising sensing materials for LPG detection, more over these composites can be tested for the detection of other organic and toxic gases.

Sensitivity of a sensor is defined as the ratio of resistance without test gas and with test gas in other words the response of the sensor in presence of the test gas to reference atmosphere. The sensitivity response of the composites is as shown in ‘Figure 7’. If $R_a$ is the initial resistance in reference atmosphere (no test gas) and $R_g$ is the resistance in test gas atmosphere, then sensitivity is given by.

$$S_g = \left[\frac{R_a}{R_g}\right]$$

Sensitivity of 20 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI is very high among all the composites, this clearly show that 20 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI is very useful in the design of the sensing device. This composite start giving the response by changing its resistance immediately after the introduction of very low concentration of test gas, the high sensitivity of this composite is due to large number of pores hence large surface area for interaction, which is revealed by ESEM. Hence 20 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI is very sensitive to detect LPG [32].
4. Conclusions
PANI / Sr$_3$(AsO$_4$)$_2$ composites are synthesized by in situ polymerization method. Characterization using FTIR spectra confirms presence of amine, rings, metal oxide groups and formation of polyaniline / Sr$_3$(AsO$_4$)$_2$ composites. X-RD confirms crystalline structural retention of Strontium arsenate in PANI during polymerization. The ESEM images shows chain / branched morphology with crystalline Sr$_3$(AsO$_4$)$_2$ and presence of capillary pores inter connected with each other. The temperature dependence conductivity is thermally activated behavior of PANI / Sr$_3$(AsO$_4$)$_2$ composites and thermal curling effect increase conductivity by increase in conjugate length of polymer. It is observed that for 20 & 30 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI change in resistance increases, this results shows that analyte gas has large surface of interaction due to surface charge formation and presence of interstitial oxygen atoms. The 20 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI composite resistance change from concentration of 925 PPMV to concentration of 22,264 PPMV is of the order of 1.49 kilo-Ohms, this range of change in resistance is very much useful in designing sensor device to convert the change resistance to electrical signal. The 20 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI composite start giving the response by changing its resistance immediately after the introduction of very low concentration of LPG, hence 20 wt% of Sr$_3$(AsO$_4$)$_2$ in PANI composite is competent material for sensor device.

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