



Room temperature liquefied petroleum gas sensor based on n-Bi₂S₃/p-PEDOT: PSS heterojunction

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Abstract

We are investigated the combination of inorganic semiconducting nanocrystalline material with most stable organic polymer layer can leads to diverse effect towards gas sensor activity. Hence, room temperature liquefied petroleum gas (LPG) sensor has been developed based on the heterojunction between chemically synthesized n-Bi₂S₃ and spin coated p-PEDOT: PSS thin layers deposited at room temperature. Both this methods are facile, low cost and suitable for large area deposition. Furthermore, this heterostructure (bi-layer) assembly has characterized using XRD, EDX, and SEM, cross sectional studies. Finally, we achieved the 64.7 % gas response at 800 ppm concentration of LPG at room temperature (27°C). The response and recovery time was calculated as 170 s and 80 s, respectively. Since, the results are designated that this heterostructure are capable for LPG sensing at room temperature (27°C).

Keywords: Room temperature, LPG Sensor, Heterojunction, n-Bi₂S₃/p-PEDOT: PSS.

1. Introduction

The lethal and explosive gas detection plays a major role in environmental air quality monitoring. A genuine- time monitoring of perilous gases and signal of fortuitous leakages is of great importance owing to the concern for safety requirements in industries and household applications. Among, the lethal, inflammable and perilous gases the liquefied petroleum gas (LPG) is applied to those hydrocarbons in which the chief component consisting as butane and propane, etc. However, they are inflammable, volatile with mixture of air and potentially hazardous due to high possibility of explosion or major accidental problem caused by leakage or by human error. Precise monitoring leakage of LPG even at low concentration it is beneficial to prevent accidental problem. It has been reported that, at the concentration up to conspicuous leakage, it is very much more than the lower explosive limit LEL of the gas in air.

Recently the application range of semiconductor gas sensors using metal oxides such as TiO₂ [1] ZnO [2], CdO [3] WO₃ and SnO₂ [4, 5], etc is spreading more and more to include the detection for LPG in last decade. There are still many critical limitations of commercial sensors based on thin film semiconductor metal oxides such as high operating temperatures and poor sensing performance. Thus increase in power consumption, limit the sensor life and portability, etc. this fundamental results are faraway from satisfactory. In particular, many researchers are dynamically engaged in developing the LPG detection but they could not reach up to the depth demand by society. Hence, there is an augmented demand towards to develop swift and precise sensors in order to detects these hydrocarbon gases upto it's lower limit and it should be upgraded in sensitivity, reproducibility, stability along with room temperature operation. In recent year, the conducting polymers found to be attractive and effective materials due to easy synthesis, room temperature

operation and relatively stable nature. This conducting polymer in combination with semiconducting inorganic material should open-up; the way to fabricate heterojunction for wide range of applications in medical and environmental field due to their electrical conductivity and sensitivity to specific photon energies or chemical species.

Earlier studies showed that the chemically deposited n-CdS, and electrochemically deposited n-type CdTe and CdSe semiconducting thin films as a heteropartner with p-type electrochemically deposited polyaniline for LPG sensing at room temperature. However, the cadmium-based chalcogenide suffers through toxicity due to inclusion of toxic, hazardous cadmium. Thus, there is a prevailing need to replace cadmium with environmentally friendly materials at domestic level as well as industrial production and environmental protection [6-8]. Amid this vision, we have been extensively studied on growth of stable and environmentally friendly nanostructured material heterostructure at comparatively low temperature has attracted curiosity, particularly towards the fabricating an electronic device including optoelectronics devices, solar cells, gas sensors, etc., and for understanding the physics of such devices. Besides, this we form the heterojunction between n-Bi₂S₃ and p-PEDOT: PSS for the detection of LPG at room temperature. Thus, the results are showed that the heterojunction is proficient for reliable sensor material.

The sensing mechanism of p-n heterojunction concept relates to the layers by forming chemical/physical contacts in which interface acts as an active region. In this case, the gas molecules are adsorbed on either side of the heterocontact are oxidized at varying rates at the heterojunction interface and influence its rectifying characteristics and change in the electrical current. Thus, the change in potential barrier height; which modifies the charge transfers characteristics [9-10]. Within the scope of the present investigation, experiments have been performed for the fabrication of heterojunction between n-Bi₂S₃ and p-PEDOT: PSS (3, 4 poly-ethylene dioxy-thiophene: poly styrene sulfonic acid). This approach has obvious advantages over conventionally fabricated gas sensors belongs to used deposition methods are eco-friendly, room temperature operation with low fabrication cost and suitable for large area deposition. Lastly, check the performance of this heterojunction (n-Bi₂S₃/p-PEDOT: PSS) towards LPG sensing at room temperature operation.

2. Experimental details

For the synthesis of Bi₂S₃ thin film, bismuth nitrate [Bi (NO₃)₃·5H₂O], thioacetamide [CH₃-CS-NH₂], triethanolamine (C₆H₅NO₃), All the chemicals were of Loba make (GR grade) and used as supplied. Also, we used commercially available PEDOT: PSS purchased from Bayer AG. Baytron HC Starck's

2.1 Deposition of n-Bi₂S₃ on fluorine doped tin oxide (FTO)

Our previously reported successive ionic layer adsorption and reaction (SILAR) method was adopted for the synthesis of n-Bi₂S₃ on fluorine doped tin oxide (FTO) coated glass substrate at room temperature (27°C) [11]. In short, separately placed cationic and anionic aqueous precursor's solutions as bismuth nitrate (3 mM/L) complexed with tri-ethanolamine (TEA) with the resultant pH~9 and thioacetamide (100 mM/L) with pH~11 adjusted by drop wise addition of dilute solution of hydrazine hydrate, respectively. The immersion time of substrate in an anionic and cationic solution was 15 s, respectively, and rinsing time in ion exchanged water was 10 s. Number of immersion cycles were optimized to get uniform film with appropriate thickness. After the deposition, the film was washed with double distilled water, dried in air and used for further deposition of PEDOT: PSS.

2.2 Deposition of p-PEDOT: PSS on n-Bi₂S₃/FTO

PEDOT: PSS was used to fabrication for heterogeneous partner with Bi₂S₃. Fig. 1 shows the molecular structure of PEDOT: PSS in which the π conjugated system is responsible for the hole transport in PEDOT. An aqueous colloidal dispersion of PEDOT: PSS (Baytron P) was purchased from Bayer AG. Baytron HC Starck's P is an aqueous dispersion of the intrinsically conductive polymer PEDOT: PSS and the formulation consists of the PEDOT: PSS ratio as 1:2.5 (by weight).

The spin coating technique was used for the coating of thin layer of p-PEDOT: PSS on previously deposited n-Bi₂S₃ thin film. This was accomplished by placing drop of PEDOT: PSS on Bi₂S₃ and spinning the sample initially with 500 rpm for 2 min followed by 4000 rpm for next 3 min. The obtained samples

were annealed at 100°C for 4 min and silver paste contact was employed on the top of PEDOT: PSS layer and kept for overnight to ensure better ohmic contact.

2.3 Characterizations

The crystal structure of Bi₂S₃ on FTO and PEDOT: PSS on FTO/Bi₂S₃ layers were examined by using X-ray diffractometer pattern (Miniflex Rigaku) with CuKα1 radiation ($\lambda=1.5406 \text{ \AA}$) in 2 θ range from 10 to 80 degree. The surface and cross-sectional morphologies of Bi₂S₃ and FTO/Bi₂S₃/PEDOT: PSS films were observed by using scanning electron microscopy (SEM, S-4800, Hitachi, 15 kV). The compositional analysis was investigated by using energy dispersive x-ray analysis coupled with SEM unit. Potentiostat/Galvanostat model Super-1000S (SAP Instruments Pvt. Ltd, Howrah, India) was used to perform the current-voltage (I-V) characteristics of the liquefied petroleum gas (LPG) sensing device at room temperature.

3. Results and discussion

3.1 Structural study

Fig. 2 shows the X-ray diffraction patterns of Bi₂S₃ film on fluorine doped tin oxide coated (FTO) glass substrate and PEDOT: PSS film on FTO/Bi₂S₃ film with removed background peaks of FTO coated glass substrates. The amorphous appearance of spectrum with tiny broad peaks for Bi₂S₃ shows the nanocrystalline nature of the film as depicted in fig 2(a). The small peaks for Bi₂S₃ film are appeared at 33.9°, 41.2°, 49.2°, 54.4°degrees for the planes (1 3 1), (0 5 1), (2 2 1) and (1 1 6) corresponds to orthorhombic crystal structure (JCPDS card no. 84-0279). The average crystallite size of film was calculated by using the following equation.

$$t = \frac{0.9\lambda}{\beta \cos \theta}$$

Where 't' is the crystal size; ' λ ' is the wavelength of X-ray used; 'b' is the angular line width of half maximum intensity; and ' θ ' is the Bragg's angle. The average crystallite size of Bi₂S₃ thin films was found to be 4.42 nm. PEDOT: PSS film declares the absence of any sharp diffraction peak indicating amorphous structure as depicted in fig 2(b).

3.2 Surface morphological and elemental study

Fig. 3a shows the surface morphology of nanostructured Bi₂S₃ on fluorine doped tin oxide coated (FTO) glass substrate shows uniform and well surface coverage with the grain size ranges between 10-30 nm. This morphology facilitates infiltration of the gas molecules inside of the sensor film bulk. From figure 3b, the blurred slurry image of small granular particles shows the presence of PEDOT: PSS layer on the top of Bi₂S₃. We believe that this slurry layer covered the whole Bi₂S₃ layer and penetrates inside the porous from top to bottom resulting in the large surface heterojunction interface would also enhance the effective surface area and enable the gas to react easily. Insight view demonstrates the cross-sectional image of entire heterojunction where clear distinction can be made for FTO, Bi₂S₃ and PEDOT: PSS layers with the thickness about 700-800 nm for Bi₂S₃ and less than 100 nm for PEDOT: PSS layer. Therefore, better metrological performances of these materials namely the detection limit, the sensitivity and the response time are expected.

3.3 Energy-dispersive X-ray spectrometry (EDS) study

Energy-dispersive X-ray spectrometry (EDS) is a technique to measuring the intensity of X-ray emission as a function of energy of X-ray photons. The energetic electrons (or photon or ions) are made incident on n-Bi₂S₃/p-PEDOT: PSS. In which an electron interacts with an atom from n-Bi₂S₃/p-PEDOT: PSS by ionizing inner shell electron. The resultant vacancy is filled by an outer electron, which can release its energy by emitting an X-ray. This produces characteristic lines in the X-ray spectrum corresponding to electronic transition involved. Since these lines are specific to a given elements and the composition of the material can be deduced. The intensity of generated X-ray is related to the concentration fraction of each element present in the target material. For the same the corresponding chemical composition of the FTO / n-Bi₂S₃ is as shown in figure 3a'. Elemental peaks of Bi, S, and Sn are clearly observed in EDX pattern for the

presence of Bi, and S from Bi₂S₃ whereas Sn is from the background substrate surface. The evidence of PEDOT: PSS on Bi₂S₃ layer was confirmed by elemental analysis as shown in figure 3b'. Inclusion of C and S as compared to FTO/Bi₂S₃ layer at lower energy scale clearly supports the presence of PEDOT: PSS.

4.3 LPG sensing of n-Bi₂S₃ / p-PEDOT: PSS heterojunction

The LPG sensing properties of n-Bi₂S₃/p-PEDOT: PSS heterojunction was studied by using our laboratory made sensor unit [12]. The current–voltage (I-V) characteristics under ambient air and under LPG environments at various gas concentrations (400 to 1000 ppm) were performed for the heterojunction films. Silver paste was used as a front ohmic contact where as FTO coated glass substrate (sheet resistance 15 Ω/□) as a back contact. The fixed voltage value was selected where the maximum change in the resistance occurred when samples exposed to the gas environment with reference to the air and the sensitivity values were calculated by using formula as follows,

$$S(\%) = \frac{I_a - I_g}{I_a} \times 100 = \frac{\Delta I}{I_a} \times 100$$

where 'I_a' and 'I_g' are the current density values in the presence of air and gas respectively. Furthermore, the response time, recovery time, and repeatability is important properties in LPG sensing study. These properties were determined by holding the junction to a fixed potential (+2.3 V) and the junction current change was recorded with time.

In the LPG sensing study initially, we check the forward biased current-voltage (I-V) characteristics of the individual n-Bi₂S₃ in presence of air (a) and in presence of 800 ppm concentration of LPG (b), Also, check the forward biased current-voltage (I-V) characteristics of the individual p-PEDOT: PSS in presence of air (c) and in 800 ppm concentration of LPG (d) as depicted in Fig. 4. The unwavering nature of the curve for individual layers in air and under exposer of LPG environment clearly demonstrates the non-sensing behaviors at room temperature (27°C).

Fig. 4 shows that the forward biased current density-voltage (J-V) characteristics and it shows drastic change in the resistance under exposed to LPG environment from 400-1000 ppm (f-j) in the voltage range from 0 to 3 V as compared to air (e) environment and attained a maximum change at +2.3 V voltage value at 800 ppm. When the LPG concentration varied from 400 ppm to 1000 ppm, the response value was enhanced from this the response is function of gas concentration after 800 ppm of gas concentration a saturation point is reached. The increase in gas response up to the saturation limit may be attributed to the decrease in charge carrier density in the active surface, with the increase in concentration of gas exposure, due to rapid adsorption of gaseous species. This causes a raise in resistance, which consequently increase the gas response. On the other hand, saturation behavior of gas response, beyond the optimum response time (the time at which gas response reaches maximum), may be explained as follows. With the duration of exposure to gas, the gas interaction with the device active layer increases. After the culmination of optimum response time, the gas adsorption into the active layer reaches a saturation state causing the saturation of gas response or decrease in gas response. Because the gas response of the heterojunction thin film depends on the reaction between the sensor interfaces with a target gas.

Fig. 5 shows the gas response verses respect to LPG concentration, the maximum gas response of 64.7% was observed at 800 ppm of LPG and then drastically decreased to 15% with further increase in the gas concentration upto 1000 ppm. This decrease in the gas response may be due to the active area of gas sensor material was up to 800 ppm this amount of gas was sufficient to form unimolecular layer which covered the whole heterojunction interface. Above 800 ppm of LPG concentration, the response was decreased drastically since the effect of active area was diminishing due to the formation of multilayers of gas molecule and heavier nature of gas molecule at the interface.

Mainly the heterojunction-based gas sensor is potential barrier dependent. When the gas molecules enter through the thin layer of p-PEDOT: PSS material and reach to the interface of junction, the change in work function of p-type PEDOT: PSS. Due to the electron transfer from n-Bi₂S₃ to p-PEDOT: PSS due to the higher value of the work function of PEDOT: PSS (5.1eV) than the electron affinity of Bi₂S₃ (4.5eV). When heterojunction is reacted with LPG then it likely seems as the dissociation of reducing molecule of LPG at surface or interface, this leads to be an increase in work function of p-PEDOT: PSS and the decrease in carrier concentration near the interface of heterojunction. This may cause the increase in potential barrier height of the heterojunction and consequently decrease the sensor current across the junction. The change in

current may be due to the chemical reaction between interface of heterojunction and adsorbed gas molecules. Tucci et al. [13] have reported that the change in the conductivity is due to the interaction of adsorbed gas molecules onto interface of heterojunction. The schematic representation of heterojunction working model of gas the sensor and their corresponding physical models (a') and (b') is as shown in Fig. The decrease in forward current with increased concentration of LPG has been attributed to the decrease in charge carrier concentration as LPG and the change in work function of the PEDOT: PSS, the doping level of derivatives of PEDOT: PSS and resistance of the PEDOT: PSS increases; when molecules reach at the interface of the heterojunction through PEDOT: PSS contrast to hydrogen gas sensors based on Pd/TiO₂ [14].

The response and recovery times are the most deciding parameters, as response time decides the instantaneity of the sensor for the incoming gas species and recovery time shows the ability of sensor to recover its original characteristics to have ready for monitoring gas sensitively in further exposure. The response and recovery time for the junction was performed at 800 ppm of LPG with a fixed potential of +2.3 V where maximum gas response was observed. As LPG was exposed (ON state) to the sensor material, the sensor response reaches upto 64.7% within 170 s (response time). As the gas is flushed out from dome by using vacuum pump and the sensor material is exposed (OFF state) to clean air, the gas response falls down within 80 s (recovery time). Furthermore, the response and recovery time was performed in order to check the reproducibility of the device for next two successive cycles which is as shown in inset of Fig 5.

The stability study is important factor towards the application of the sensor at the industrial level. This was performed upto 12 days at room temperature by keeping fixed voltage (+2.3 V) and LPG concentration (800 ppm) where the maximum gas response was observed. The variation in the gas response against time (days) is illustrated in Fig 5. The performance of the gas response was remained stable for first two days then decreased to 10% of initial value within next four days and remains stable thereafter. Hence, we can conclude that the n-Bi₂S₃ / p-PEDOT: PSS heterojunction device is able to place for a trustworthy as a sensor material for LPG sensing at room temperature.

4. Conclusions

With this regards we have successfully developed heterojunction between chemically deposited n-Bi₂S₃ and p-PEDOT: PSS layers at room temperature with simple, inexpensive chemical methods at room temperature with lower manufacturing cost; without any heat treatment. This heterojunction device was effectively used to sense the liquefied petroleum gas (LPG) at room temperature (27°C) with the remarkable gas response of 64.7% at 800 ppm concentration of LPG. The observed stability along with short response and recovery times clearly demonstrated the ability of the developed heterojunction device for wide domestic as well as industrial application towards human safety.

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Figure captions

Fig.1. The molecular structure of PEDOT: PSS

Fig.2. The X- Ray diffraction patterns of (a) Bi_2S_3 film on FTO coated glass substrate, and (b) PEDOT: PSS thin film on FTO/ Bi_2S_3 film with removed background peaks of FTO.

Fig.3. The scanning electron micrographs of (a) Bi_2S_3 film on FTO coated glass substrate, and (b) PEDOT: PSS thin film on FTO/ Bi_2S_3 with elemental analysis of (a') n- Bi_2S_3 and (b') FTO/n- Bi_2S_3 / p-PEDOT: PSS heterojunction. Inset shows the cross-sectional, scanning electron micrographs of FTO/ Bi_2S_3 / PEDOT: PSS heterojunction

Fig.4. Forward biased $I-V$ characteristics of individual n- Bi_2S_3 (a-air, b-gas) and p-PEDOT: PSS (c-air, d-gas) at 800 ppm LPG concentration. Forward biased $I-V$ characteristics of n- Bi_2S_3 /p-PEDOT: PSS heterojunction in (e) air and at various concentrations of LPG (f-j) (f) 400 ppm, (g) 500 ppm, (h) 600 ppm, (i) 800 ppm, (j) 1000 ppm. Inset shows the plot of variation in gas response (%) versus LPG concentration (ppm) of n- Bi_2S_3 / p-PEDOT: PSS heterojunction at 2.3 V.

Fig.5. The plot of gas response (%) versus variation in time (days) for the device at 2.3 V under 800 ppm of LPG. Inset shows the plot of repeatability of gas response (%) versus time (s) for the n- Bi_2S_3 / p-PEDOT: PSS heterojunction layer under 800 ppm of LPG at a fixed voltage (2.3V).

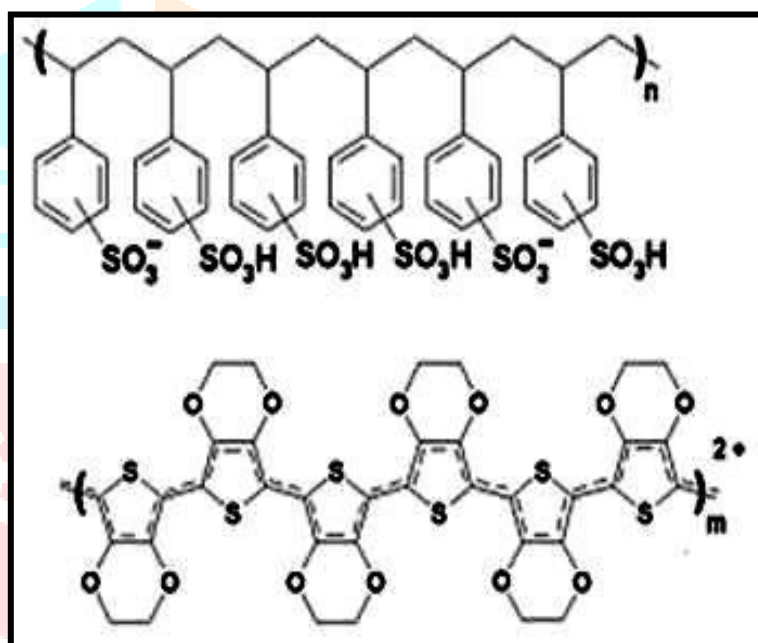


Fig 1

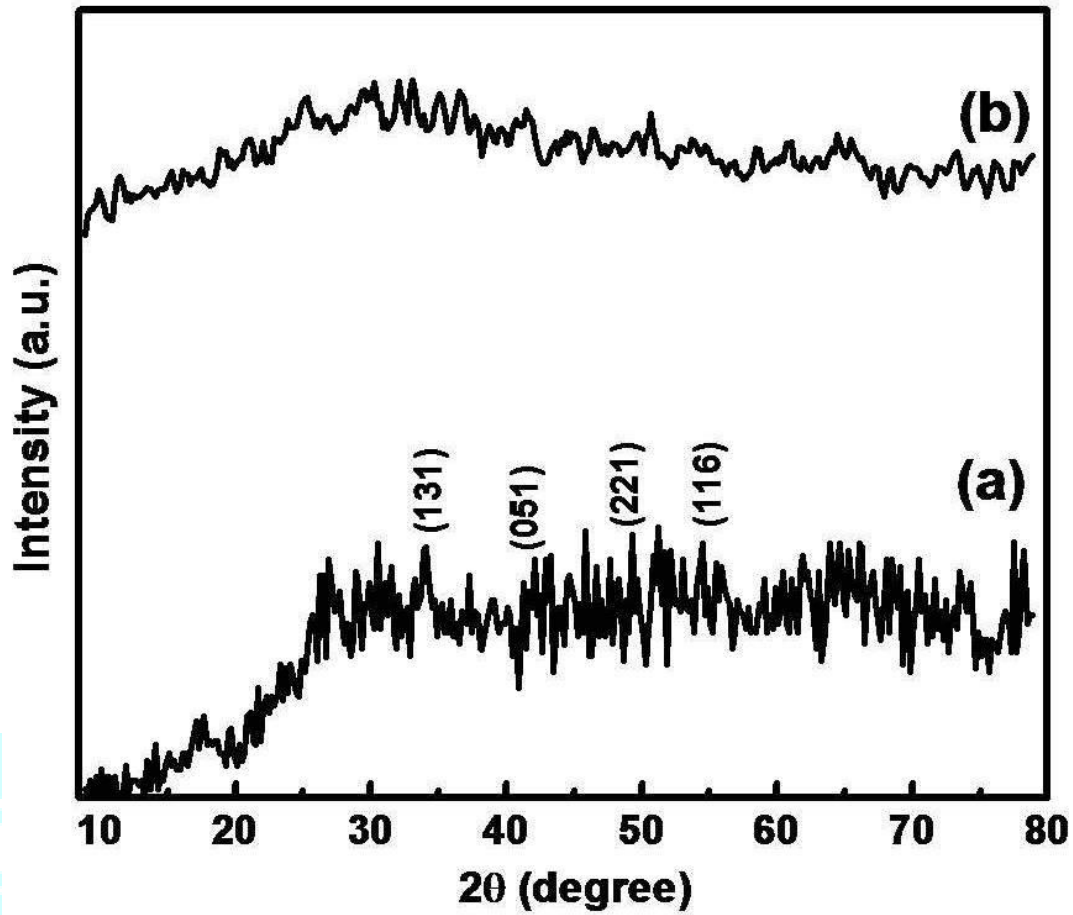


Figure 2

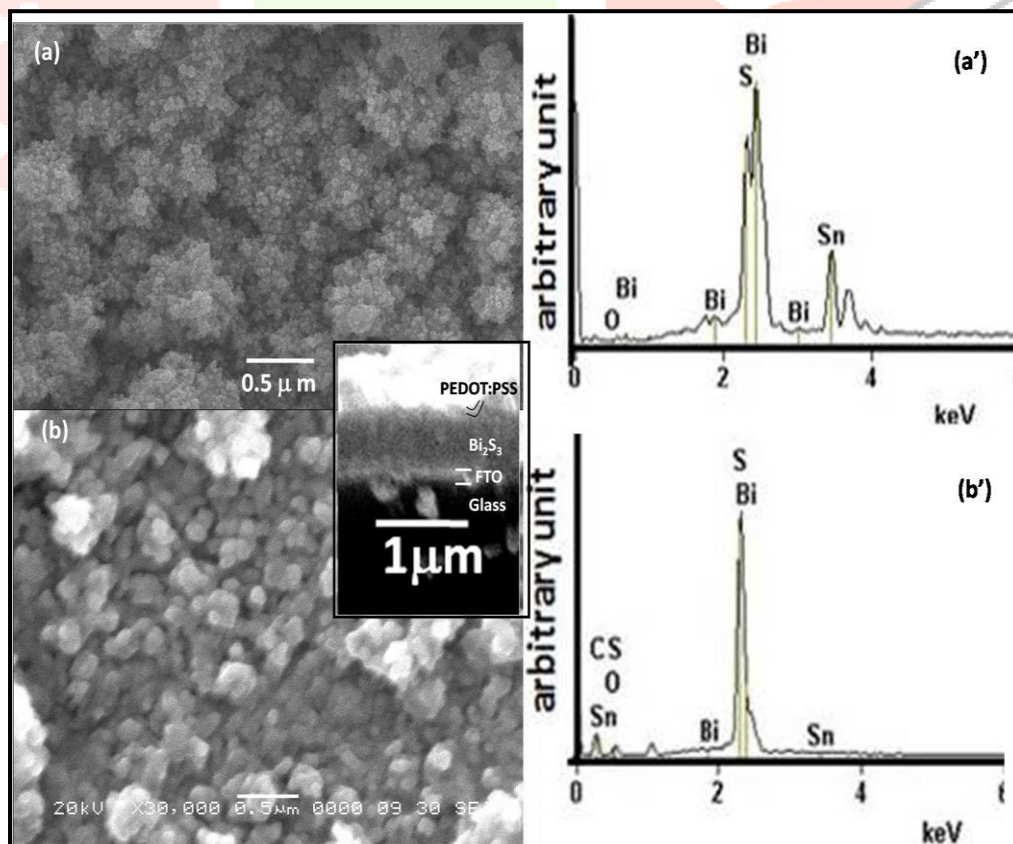


Figure 3

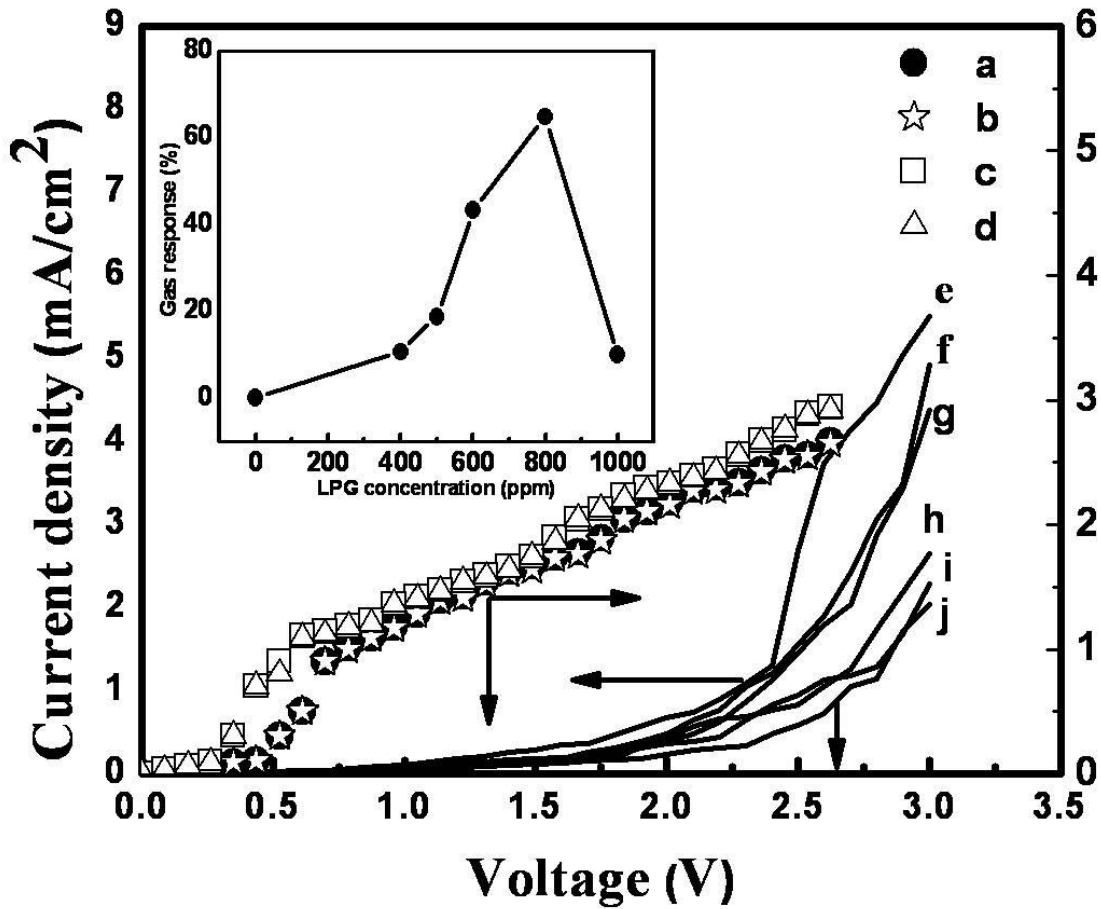


Figure 4

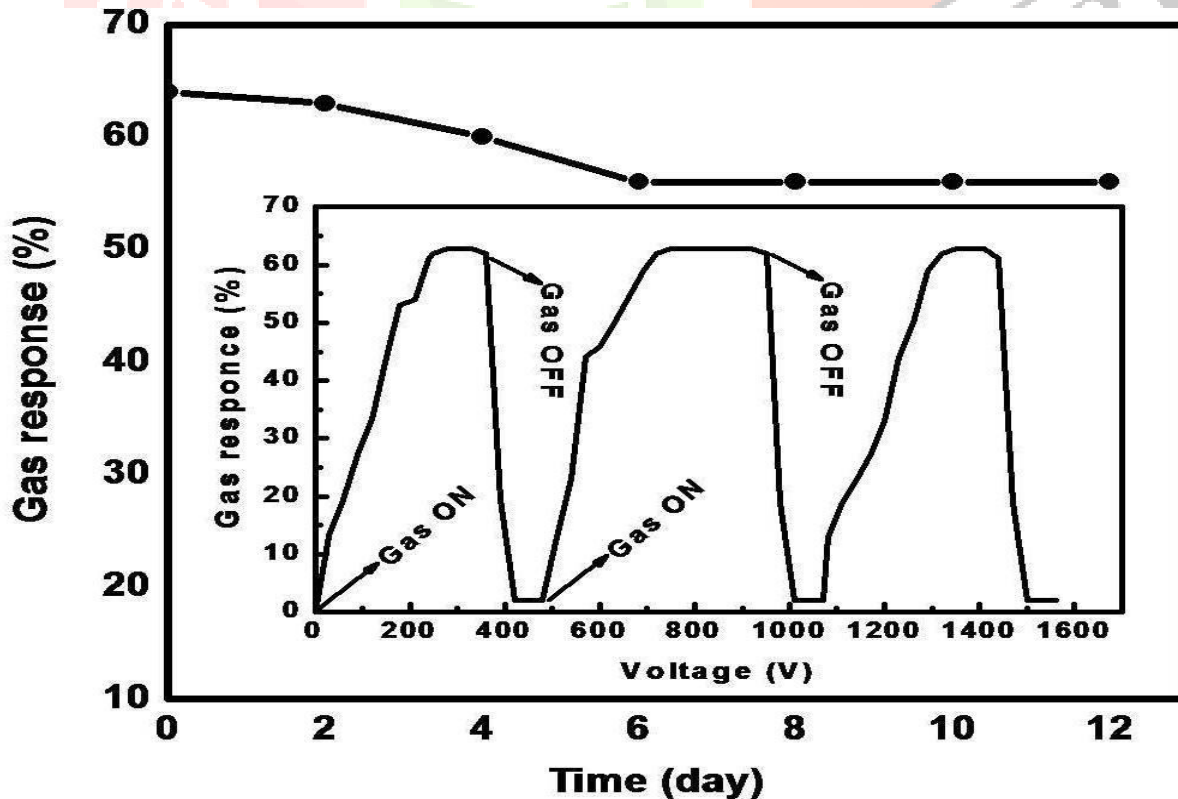


Figure 5