## CHAPTER- III

SYNTHESIS AND CHARACTERIZATION OF n-CdS/p-PEDOT:PSS AND n-CdS/p-PbS HETEROJUNCTION AND ITS APPLICATION AS A LPG SENSOR

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III.A Synthesis and characterization of n-CdS/p-PEDOT:PSS nanoheterojunction and its application as a LPG sensor

III.A.1 Introduction

Among different gases, liquefied petroleum gas (LPG) is inflammable and hazardous gas. The leakage of the LPG may lead to a serious accident and hence, there is a prevailing need to detect LPG at low concentration level before causing serious accident. Recently, heterojunction concept has been used for detecting LPG at room temperature. Early studies related to organic–inorganic heterojunction generally involved polyaniline based heterojunctions at room temperature [1-3]. It has been well documented that the conducting polymers are sensitive to environmental compositions. Among the commonly used conducting polymers, poly(3,4-ethylenedioxythiophene: poly (styrene sulfonic acid) (PEDOT:PSS) has attracted a lot of attention in recent years due to its excellent properties such as long-term stability, high conductivity and is commonly accepted to be more environmentally stable than other conducting polymers.

In the present work, effort has been put forth for the formation of uniform p-PEDOT:PSS shell on n-CdS nanowires to form the nanoheterojunction device to sense LPG. The advantages includes (i) room temperature synthesis of CdS nanowires, (ii) use of simple and low cost chemical methods, (iii) formation of heterojunction with high surface area, (iv) enough space to adsorb and deadsorb gas molecules through porous network, (v) room temperature LPG detection, and (vi) applicable for large area production.

III.A.2 Experimental

The synthesis of Cd(OH)2 and CdS nanowires was done by using cadmium chloride(CdCl2) and sodium sulphide (Na2S) and ammonia as a complexing agent by using simple chemical route. All the chemicals used, were of Loba chemicals (GR grade) and used as supplied. The commercially available PEDOT: PSS was purchased from Bayer AG. Baytron HC Starck’sand used in optimized proportion with deionized water. p-PEDOT:PSS was coated on FTO/n-CdS film by using dip coating technique. The silver paste was used for the contact such that FTO/n-CdS/p-PEDOT: PSS/ Ag device can form.

III.A.2.a Substrate cleaning

The contaminated surface of substrates provides nucleation sites facilitating growth resulting into non-uniform films, so the extreme cleanliness of the substrate is
important in chemical deposition of thin films. In present work, we have used fluorine doped tin oxide (FTO) coated glass slides of sheet resistance (15 ohm/sq.cm) as the substrates for the synthesis of thin films. Initially, the substrates were cleaned with laboline and double distilled water. Then, the substrates were cleaned ultrasonically for 15 minutes in ethanol solution, and finally the substrates were cleaned with double distilled water twice and then used for the deposition.

III.A.2.b Deposition of CdS nanowires

Deposition of Cd(OH)$_2$ nanowire thin film was performed by using simple chemical bath deposition (CBD) at room temperature (27 $^\circ$C) on fluorine doped tin oxide (FTO) coated glass substrates. Precursor from an aqueous medium containing 0.1 M/L CdCl$_2$ complexed with ammonia was used for the deposition of thin film consisting of nanowires. Initially, white precipitate of Cd(OH)$_2$ was observed during the formation of cadmium–ammonia complex which gets dissolved after further addition of ammonia having the resultant pH of 12. For the deposition of Cd(OH)$_2$ film, FTO coated glass substrate was immersed vertically along the wall of the beaker containing precursors. After 21 hrs of deposition, the white Cd(OH)$_2$ film was deposited on to the substrate which was taken out, rinsed with double distilled water and dried in air. In order to form CdS, Cd(OH)$_2$ thin film covered on FTO substrate was immersed in the beaker containing 0.01 M/L sodium sulphide (Na$_2$S) solution at pH of 7.6 and kept for 2 hrs. The recent reports reveals the conversion of Cd(OH)$_2$ to CdS films using ion-exchange method. The ion-exchange reaction is possible due to more negative solubility product of CdS ($10^{-28}$) than that of Cd(OH)$_2$($10^{-14}$) [4,5].

Reaction mechanism

The Cd(OH)$_2$ nanowires were grown through a simple wet chemical route. Cadmium ions upon meeting sufficient OH$^-$ gives white precipitate as long as solubility product of [Cd$^{2+}$][OH$^{2-}$] is greater than the solubility product of Cd(OH)$_2$ (2×10$^{-14}$) at room temperature (27 $^\circ$C). Since hydrated cadmium ion complexes were transferred to cadmium hydroxide through the stepwise replacement of water molecules.

\[
\text{CdCl}_2 + \text{NH}_3 + 2\text{H}_2\text{O} \rightarrow \text{Cd(OH)}_2 + \text{NH}_4\text{Cl} + \text{HCl}
\] (1)

The CdS films were obtained by reaction with sulfur ions source. Interdiffusion of S$^{2-}$ ions occurs through Cd(OH)$_2$ films, the outer covering layer of CdS begin to form towards the inner side by replacing hydroxyl group with sulfur ions until white [Cd(OH)$_2$] completely converted to yellowish CdS. This
transformation is possible due to more negative solubility product of CdS than that of Cd(OH)$_2$. Complete transformation was confirmed by optimizing reaction time with sulfur source and further characterizations. The reaction for the formation of CdS from Cd(OH)$_2$ is summarized as follows.

$$\text{Cd(OH)}_2 + \text{Na}_2\text{S} \rightarrow \text{CdS} + 2\text{NaOH} \ (2)$$

### III.A.2.c Deposition of PEDOT:PSS shell on CdS nanowires

The shell formation of PEDOT:PSS on CdS nanowires was performed by using simple dipping technique. Commercially available PEDOT:PSS solution from Baytron (HC Starck’s Clevios PH1000) was used to form the shell. At each time, each volume of PEDOT:PSS::H$_2$O was ultrasonicated for 1 h. The PEDOT:PSS::H$_2$O ratio, ultrasonication, dipping and heating times were optimized in order to get uniform and thin layer coating of PEDOT:PSS on CdS nanowires towards better gas sensing performance. Different ratios of PEDOT:PSS::H$_2$O was used and the ratio 1:4 was found to be optimal. For this, PEDOT:PSS containing 80% water was coated on FTO/CdS film by using dip coating technique. A single dip consists, FTO/CdS film was dipped vertically into PEDOT:PSS::H$_2$O solution for 2-3 seconds and taken out vertically. After 4 to 5 such a dips in the intervals of few seconds, a very thin, homogeneous layer of PEDOT:PSS was coated on CdS nanowires. After coating, the dip coated film of FTO/CdS/PEDOT:PSS was heated at 100°C for 10 min in air.

### III.A.2.d Characterization techniques

The surface morphology and elemental composition was examined by using scanning electron microscopy (SEM) (JEOL 6360A) coupled with energy-dispersive X-ray analyzer (EDAX) attached to the SEM unit. Transmission electron microscopy (TEM) images were recorded by using conventional transmission electron microscopy (TEM, JEM 2000EX, JEOL, Tokyo, Japan). Fourier transform infrared (FT-IR) studies were performed by using model FT-IR (Perkin–Elmer) spectrum in the wave number 500–4000 cm$^{-1}$.

The gas sensing properties were recorded under forward biased current density–voltage ($J$–$V$) characteristics between 0 and 1.5 V by adopting the same method mentioned in chapter II.D.1 and II.D.2.

### III.A.3 Results and discussion

#### III.A.3.a Surface morphological and compositional studies

Fig.III.A.1 (a) and (b) shows SEM images under different magnifications for CdS nanowires with magnifications of 500 nm and 5 µm, respectively whereas
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fig.III.A.1 (c) and (d) for PEDOT:PSS coated CdS nanowires with magnifications of 500 nm and 5 µm, respectively. It clearly shows the formation of nanowires with highly porous structure. This type of novel surface morphology is very useful for gas sensing purposes.

**Fig.III.A.1** The scanning electron micrographs of n-CdS film on FTO coated glass substrate with scale bar of (a) 500 nm, and (b) 5µm, respectively and p-PEDOT:PSS layer coated n-CdS nanowires with scale bar of (c) 500 nm, and (d) 5 µm, respectively.

From Fig.III.A.1 (a), it is clearly observed that one rope with diameter ranging from 50 to 130 nm composed of several nanowires of CdS that are aggregated to form the bundles. At lower magnification, the random distribution of CdS nanowires spread on FTO substrate with enough porous is observed (Fig.III.A.1(b)). The higher magnification image clearly depicts the formation of blurred CdS nanowires confirming uniformly covered slurry of PEDOT:PSS over the CdS nanowire (Fig.III.A.1 (c)). At lower magnification, it is observed that some polymer slurry was stacked at the junction area of nanowires (Fig.III.A.1 (d)). The uniform growth of p-type polymer shell on the n-type nanowires results into the formation of high surface area p–n junction at the nano level and hence, the formation of nanoheterojunction. Such novel morphology provides high surface area nano network allowing enough room to adsorb and de-adsorb gas molecules easily at the interface which can finds application as the gas sensor.
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To ascertain uniform growth of PEDOT:PSS shell on the CdS nanowires, TEM analysis has been performed. Fig.III.A.2 (a and b) shows TEM images of CdS nanowire and PEDOT:PSS shell on CdS nanowires. Comparing both the images, clear distinction can be made for dark coating of PEDOT:PSS shell on CdS surface with average thickness between 15 and 20 nm. These results are consistent with SEM results which supports the coating of slurry PEDOT:PSS polymer layer on the CdS nanowires towards the formation of nanoheterojunction.

In energy-dispersive X-ray analysis (EDAX), the intensity of X-ray emission is measured as a function of energy of X-ray photons. For this, the energetic electrons (or photon or ions) are made to incident on n-CdS/p-PEDOT:PSS. These electrons interact with an atom from n-CdS/p-PEDOT:PSS by ionizing inner shell electron. The resultant vacancy is filled by an outer electron, which can release its energy by emitting a characteristic X-ray, which produces characteristic X-ray line spectrum corresponding to electronic transition of particular element. Fig.III.A.3 (a and b) shows elemental spectrum of bare CdS nanowire and PEDOT:PSS shell coated on CdS nanowires. The Cd and S peak in Fig.III.A.3 (a) confirms the existence of CdS. Comparing elemental spectrum of bare CdS with PEDOT:PSS shell on CdS nanowires (Fig.III.A.3. (b)), enhancement in ‘S’ peak intensity is observed which is due to the PEDOT:PSS shell formation on CdS nanowires. The carbon content in the PEDOT:PSS shell coated CdS nanowires gives rough confirmation towards the
existence of PEDOT:PSS layer on CdS nanowire. The appearance of Sn, Si, sodium (Na) and magnesium (Mg) is from FTO coated glass substrate. The existence of gold (Au) is from evaporated Au on top of film in order to get good quality SEM images.

III.A.3.b Fourier transform infrared studies of CdS and PEDOT:PSS coated CdS

CdS nanowires and PEDOT:PSS shell on CdS nanowires are characterized by FT-IR spectroscopy (Fig.III.A.4). For CdS sample (Fig.III.A.4.(a)), the peak at 3522 cm\(^{-1}\) is due to traces of O-H stretching of hydroxyl group which may be attributed to smaller content of remaining hydroxide during chemical conversion of Cd(OH)\(_2\) to CdS. The peak at 1384.89 cm\(^{-1}\) attributed to C-C stretching in plane modes because of carbon from surface contamination or from used chemical impurities. The medium peak at 858.32 cm\(^{-1}\) is attributed to C-Cl stretching in group of alkyl halides due to used cadmium chloride source. The presence of C=C bond of aromatic hydrocarbon and out of plane ring bending rather than C-H out of plane bonding is confirmed by the peak at 723.31 cm\(^{-1}\).

Fig.III.A.4 (b) shows the FTIR spectrum of PEDOT:PSS shell on CdS nanowires. The spectrum presented the peak 1384.89 cm\(^{-1}\) attributed to C-C stretching in plane modes. The widening of peak around 1550–1400 cm\(^{-1}\) as compared to bare CdS is assigned to thiophene ring or due to C-C and C=C stretch of quinoidal structure. The peaks at 1168.86 and 1128.36 cm\(^{-1}\) are characteristics absorption of SO\(_3^+\) indicates the presence of sulfur from sulphonated PEDOT:PSS layer. The peak at 979.84 cm\(^{-1}\) is attributed to oxyethylene ring deformation or further vibrations from...
the C-S bond in thiophene ring. The peak at 721.98 cm\(^{-1}\) is attributed to the presence C=C bond for aromatic hydrocarbon. More confirmation of thiophene can be done due to C-S bond in thiophene ring which can be seen by the appearance of peaks at 1006 and 673.16 cm\(^{-1}\)[6,7].

![FTIR Patterns](image)

**Fig.III.A.4** The FTIR patterns of (a) CdS nanowires, and (b) PEDOT:PSS coated CdS nanowires

### III.A.3.c LPG detection at n-CdS/ p-PEDOT:PSS nanoheterojunction

The FTO/n-CdS/p-PEDOT:PSS/Ag nanoheterojunction device was formed by making silver contact on p-PEDOT:PSS layer as a front contact and FTO served as back contact. The chemically deposited CdS nanowires and PEDOT:PSS show unintentionally doped n and p-type conductivities [8-10]. The current density–voltage (J–V) curves between the p-PEDOT:PSS and n-CdS nanowires suggest the formation of p–n junction due to shell formation of thiophene on CdS nanowires. The formed nanoheterojunction was used as a sensor material towards LPG. The sensing behavior was tested by observing current density–voltage (J–V) characteristics under the exposure of different concentration of LPG with respect to air. The schematic presentation of shell formation and nanoheterojunction device is as shown in fig III.A.5.
The forward biased current density–voltage (J–V) characteristics of the heterojunction in air and under various concentrations of LPG (300–1500 ppm) are depicted in Fig.III.A.6. The change in current densities under different LPG concentrations with respect to air clearly demonstrates the sensing properties of the formed nanoheterojunction. As the junction was exposed to LPG, the forward current density was linearly increased up to certain limit. From J–V characteristics, the maximum change in the current-density was observed at 900 ppm concentration of LPG under the bias voltage of 1.5 V. With further increase in gas concentration to 1500 ppm, the decrease in the current density was observed. Under different LPG environments, as compared with air, the maximum change in current was observed at applied voltage of 1.5 V. At this voltage gas response (S) was calculated using relation.

\[ S \% = \frac{I_g - I_a}{I_a} \times 100 = \frac{\Delta I}{I_a} \times 100 \]  

(3)

where, \( I_a \) is current density in air and \( I_g \) is current density in gas environment.

The gas response of the n-CdS/p-PEDOT:PSS nanoheterojunction at various concentrations of LPG at an applied voltage of 1.5 V are shown in inset of fig.III.A.6. The gas response increases from 35.7% to 58.9% with change in LPG concentration from 300 ppm to 900 ppm. The maximum response of 58.9% was observed at 900
ppm of LPG due to single molecular layer of gas molecules formation at the interface; interacting more actively at the interface and thus, the decrease in height of potential barrier giving rise to larger response value.

![Graph](image)

**Fig.III.A.6** Forward biased I–V characteristics of FTO/n-CdS/p-PEDOT:PSS nanoheterojunction in air and at various concentrations of LPG as 0 ppm (air), 300 ppm, 600 ppm, 900 ppm, 1200 ppm, and 1500 ppm. Inset shows variation in gas response (%) vs. LPG concentration (ppm) of n-CdS/p-PEDOT: PSS nanoheterojunction at 1.5 V.

With further increase in the gas concentration above 900 ppm, a decrease in response ($S = 40\%$; 1500 ppm) value was observed. This is due to formation of multilayer of gas molecules i.e. saturation of LPG molecule at the interface which reduces the active surface area; responsible for increases in potential barrier height at the interface or also, might be due to recombination of charge carriers.

The reversibility of the heterojunction was tested from response transient measurements of the heterojunction. **Fig.III.A.7** shows the response transient curves for first two exposures to LPG at fixed voltage of 1.5 V and 900 ppm of LPG. The n-CdS/p-PEDOT:PSS nanoheterojunction shows good reversibility to LPG that has shown maximum response of 58.9%. The response transient curve provides information of response and recovery times of heterojunction. The response time is
defined as time at which the current of the heterojunction reaches 90% of the saturation value on exposure of LPG and recovery time is defined as the time required for recovering the 90% of the original current of the heterojunction.

![Gas response vs. time (s) of n-CdS/p-PEDOT:PSS heterojunction at fixed voltage of 1.5 V at 900 ppm of LPG concentration.](image)

When sensor is exposed to LPG, the sensor reaches the maximum response of 58.9% with response time of 126 s. When sensor exposed to fresh air, removal of LPG molecules shows recovery of the sensor with recovery time of 109 s. The response time observed is still high which might be due to the penetration of gas molecules takes time to move towards interior of the film from top to bottom. The observed high value of recovery time is detachment of gas molecules takes time from interior of film. The repeatability test was performed by exposing the junction to fresh air followed by exposure to LPG. The device resulted into good reversibility with response and recovery times of 147 s and 128 s, respectively.

The stability of the heterojunction is the most important factor for the industrial level manufacturing of the gas sensor device. The stability study for n-CdS/p-PEDOT:PSS nanoheterojunction was carried out over 9 days. Fig.III.A.8 shows the variation of gas response against the number of days. It is clear that gas response falls to 55.3% value and remains stable even after 9 days showing 93.88% stability.
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III.A.4 Conclusions

The simple, low cost and room temperature chemical route was successfully employed to deposit n-CdS nanowires onto FTO coated glass substrate followed by p-PEDOT:PSS shell formation by dip coating method. The used chemical methods are applicable for large area sample formation. The n-CdS/p-PEDOT:PSS nanoheterojunction with high surface area was successfully demonstrated as liquefied petroleum gas (LPG) sensor with gas response of 58.9% under the exposure of LPG (900 ppm) which can operate at room temperature (27 °C). The device shows low values of response and recovery times and having decrease in response value upto 2% after four days and remains stable thereafter. This study clearly demonstrates the possibility to use the n-CdS/p-PEDOT:PSS nanoheterojunction for the fabrication of room temperature gas sensing device by low cost chemical method.

All these results are published in Journal of Alloys and Compounds [11].
III.B Synthesis and characterization of n-CdS/p-PbS nanoheterojunction and its application as a LPG sensor

III.B.1 Introduction

The wide spread uses of LPG requires fast and selective detection of LPG to precisely measure the leakage in order to prevent the occurrence of accidental explosions. In the recent years, many efforts have been put forth for metal oxide based gas sensors such as ZnO, TiO$_2$, Fe$_2$O$_3$, SnO$_2$, CdO, and NiO [12]. The room temperature LPG sensors are mainly based on heterojunction formation with one of the material as polyaniline (PANI) [13, 14]. Attempts have made to replace PANI by stable p-type quaternary kesterite Cu$_2$ZnSnS$_4$ (CZTS). The microcrystalline CZTS have synthesized by complex sputtering method followed by sulfurization process and used with structure p- CZTS/n-ZnO as room temperature LPG sensor [15].

Recently, nanostructures such as nanowires, nanotubes, nanorods etc. have been an interesting in researchers due to their importance in basic scientific research and its potential in technological applications. They are also expected to play important roles in optoelectronic, electrochemical devices and gas sensors [16]. Wide efforts have been taken for the synthesis of the semiconducting nanomaterials with different structures such as nanorods [17], nanowires [18], nanotubes [19] etc. because of their size and dimensionality dependence of functional properties. Nanoheterojunction is the heterojunction formed between two semiconductors in nanostructure form. Gong et al. have shown that nanoheterojunction effectively enhances the surface area and resulted into improved gas response [20].

In the present study, attempt has been made to coat PbS nanoparticles onto the surface of CdS nanowires to develop nano-heterojunction (NHJ) at room temperature (27 °C) by using simple and less expensive chemical routes. The n-CdS/p-PbS NHJ is successfully demonstrated to use as a LPG sensor at room temperature (27 °C). The LPG sensing properties have been studied in detail and the results are discussed.

III.B.2 Experimental

III.B.2.a Synthesis of CdS nanowires

CdS nanowires were synthesized onto fluorine doped tin oxide (FTO) coated glass substrates by sulfurization of Cd(OH)$_2$ nanowires based on negative free energy formation. The process of synthesis of Cd(OH)$_2$ nanowires and conversion of Cd(OH)$_2$ nanowires into CdS nanowires is described in III.A.2.b.
III.B.2.b Synthesis of PbS nanoparticles onto CdS

PbS nanoparticles were chemically enchased on CdS nanowires by using successive ionic layer adsorption and reaction (SILAR) technique at room temperature (27 °C). The 3 mM/L lead nitrate [(Pb(NO₃)₃] was used as a cationic precursor at pH of 9 and 2 mM/L sodium sulphide (Na₂S) solution was used as an anionic precursor at pH of 11. One SILAR cycle consists of four steps: (1) adsorption of lead species for 20 s, (2) rinsing with distilled water for 10 s to remove excess adsorbed or loosely bounded lead species, (3) immersion of substrate in Na₂S solution to react pre-adsorbed Pb²⁺ ions with S²⁻ ions for 15 s to form stable PbS, and (4) rinsing with distilled water for 10 s to remove excess or unreacted species or powdery PbS particles. The 8 to 10 immersion cycles were optimized to get the complete coverage of PbS nanoparticles onto CdS nanowires to form better nano-heterojunction towards enhanced gas sensing performance [21].

III.B.2.c Characterization techniques

The characterizations of n-CdS, p-PbS, n-CdS/p-PbS were done by the same way as described in III.A.2.d. The structural properties of the films were studied by using X-ray diffractometer (D8Advance, Bruker AXS). The gas sensing properties of n-CdS/p-PbS NHJ were studied on the home made gas sensor unit.

III.B.3 Results and discussion

III.B.3.a Structural studies

Fig.III.B.1 (a-c) shows X-ray diffraction (XRD) patterns of CdS, PbS and PbS enchased CdS films. The peaks marked by stars are due to contribution from FTO substrates. XRD pattern of CdS films (Fig.III.B.1(a)) shows the peaks corresponding to (111), (117), (022), (200), (220), (222),(202), (331), and (420) planes of CdS with cubic crystal structure [22]. The XRD pattern of PbS film on FTO coated glass substrate shown in Fig.III.B.1 (b). The XRD pattern shows peaks (115), (118), (025), (026), (134), (229), (042) and (249) indexed to PbS with hexagonal crystal structure [23]. Fig.III.B.1(c) shows XRD pattern of PbS deposited CdS films. Peaks corresponds to (117), (118), (025), (026), (134), (229), (042) and (249) appeared in PbS are also appeared in PbS coated CdS which is better support for the formation of PbS particles on CdS nanowires whereas (111), (200), (220), (222), (202), (311), and (420) supports the existence of CdS material which was below PbS nanoparticles.
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Fig.III.B.1 The XRD patterns of (a) CdS (b) PbS and (c) CdS/PbS on FTO coated glass substrate.

III.B.3.b Surface morphological studies and elemental analysis

The FE-SEM images of CdS and PbS coated CdS films are shown in the Fig.III.B.2 (a, b). From Fig.III.B.2 (a), it is clearly observed that CdS deposited in the form of nanowires on the FTO surface. The average diameter of nanowires is about 150 nm. It has observed that, each nanowire composed of bundles of several smaller nanowires of size about 20 nm. Fig.III.B.2 (b) shows the CdS nanowires surface coating with PbS nanoparticles. The average particle size of PbS is about 70-100 nm. The PbS nanoparticles enchased CdS nanowires forms nanoheterojunction between PbS and CdS interface. Such nanoheterojunction may find useful application in gas sensor, which form high interface surface with porous structure and allows enough room to adsorb and de-adsorb gas molecules easily at the interface.

The EDAX analysis of CdS and PbS coated CdS nanowires on FTO coated glass substrates was carried out. The elemental analysis confirms the formation of CdS on FTO (Fig.III.B.2 (c)) due to presence of cadmium (Cd), and sulphide (S) peaks, whereas presence of lead (Pb) and sulphide (S) peaks confirms PbS coating on CdS (Fig.III.B.2 (d)). The inclusion of tin (Sn) is from FTO coated glass substrate.
whereas presence of silicon (Si), sodium (Na) and magnesium (Mg) is from glass substrate. The existence of gold (Au) is from evaporated Au on top of film in order to get good quality SEM images. Presence of oxygen is mainly attributed from surface contamination which is usually appeared in chemically deposited films. EDAX results supports well with XRD results.

![FE-SEM images](image)

**Fig.III.B.2** FE-SEM images of (a) CdS (b) CdS coated PbS and elemental analysis of (c) CdS, and (d) CdS coated PbS

### III.B.3.c LPG sensing properties of n-CdS/p-PbS nanoheterojunction

The chemically deposited CdS and PbS shows p and n-type conductivities respectively. The formation of heterojunction between CdS and PbS was tested by coating Ag paste on PbS layer. The complete device (FTO/n-CdS/p-PbS/Ag layer) is designed and current density-voltage (J-V) curves for the devices were tested. Fig.III.B.3 shows schematics of proposed sensor device with the structure FTO/n-CdS/p-PbS/Ag. The non-ohmic behavior of the J-V curve indicates the formation of p-n heterojunction (shown in inset of Fig.III.B.4) in the voltage range of 1.05 to -1.0 V. Low value of current density in reverse bias p-n junction is mainly attributed to non-diffusion of silver paste from top to bottom otherwise device get shortened and should represent ohmic behavior (which is not in the present case).
The formed p-PbS/n-CdS NHJ was tested as a sensor towards liquefied petroleum gas (LPG) at room temperature (27 °C).

For this, forward biased J-V characteristics were studied for the n-CdS/p-PbS NHJ in air and under different LPG concentrations. The electrical current densities of heterojunction in air (I_a) and in the presence of LPG (I_g) were measured at a fixed voltage and following equation was used to calculate the gas response.

$$ S \% = \frac{I_g - I_a}{I_a} \times 100 = \frac{\Delta I}{I_a} \times 100 \quad (4) $$

Fig.III.B.4 depicts J-V characteristics of n-CdS/p-PbS NHJ in air (a) as a reference and under the atmosphere of various concentrations of LPG (b-f) from 300-1500 ppm. After exposed of junction towards LPG, the forward current enhances with LPG concentration. The maximum change in the current density was observed for 1200 ppm concentration of LPG at 1 V.

The gas response at various concentrations of LPG was calculated at a fixed voltage of 1V and is shown in Fig.III.B.5. The gas response was increased from 28.4% to 60.7% with increase in LPG concentration and attained maximum at 1200 ppm. This may be due to unimolecular layer of gas molecules would be expected to form on the interface, which would interact with the interface more actively, giving rise to higher response. Above 1200 ppm, a decrease in response value was observed.
at 1600 ppm (0.16 vol.%) which may be due to the formation of multilayer of gas molecules at the interface of the junction, or increase in potential barrier height at the interface or may be due to recombination of charge carriers [24].

Fig.III.B.4 J-V characteristics of heterojunction (a) air (b) 300 ppm (c) 600 ppm (d) 900 ppm (e) 1200 ppm (f) 1500 ppm of LPG

Fig.III.B.5 Gas response at various concentrations of LPG at a fixed voltage 1V
III.B.3.d LPG sensing mechanism

A very few reports are available for the in-depth understanding of the LPG sensing mechanism. Lupan et al. have listed the effect of different parameters on oxide based nanowire sensor that can acts as key parameters on the sensing mechanism which are as follows: the nanowires (NW’s) diameter, aspect/ratio of the individual NWs, gas induced changes in the depletion region, donor impurities in the NWs, the surface potential, adsorption/desorption enthalpy, surface functionalization or charged surface states temperature of operation and ambient relative humidity [25]. They have pointed out that the ZnO NW’s diameter was the major contribution on the selectivity and gas response. Furthermore, they have shown the effect of O$_2$ is dominant at room temperature operation [26]. Similar type of adsorption phenomenon was studies by Chai et al. for functionalized individual ZnO microwire for natural gas detection [27]. Present study deals with complete inorganic semiconducting nanomaterials as PbS and CdS and their nano-heterojunction formation where gas induced changes in the depletion region may play important role. In the heterojunction based studies towards LPG sensing, strong support for the mechanism based on change in barrier height and thus the depletion region width under LPG environment was proposed by Patil et al. This was explained by measuring experimentally junction capacitance for p-Polyaniline/p-PbS heterojunction and thus the change in potential barrier height. In the present investigation, we have checked the effect of LPG concentration towards the change in current density which is attributed to change in depletion region width and thus the potential barrier height. Fig.III.B.6 (a) represents the schematic of the sensor with the device structure FTO/n-CdS/p-PbS/Ag contact. Fig.III.B.6 (b) and (c) show the physical models of heterojunction in order to explain the change in barrier height under air, and LPG atmosphere, respectively. Decreased barrier height ($\Phi$) of n-CdS/p-PbS NHJ after exposure of LPG may be because of following reasons (i) the increase in charge carriers, decreases resistance of p-PbS. Hence forward biased current of nano-heterojunction increased, (ii) interaction of reducing LPG molecules with the interface of nano-heterojunction changes the work function of p-PbS and (iii) it is n-CdS/p-PbS barrier that controls the current in the presence of LPG.

Similar mechanism was proposed for poly (o-anisidine)-SnO$_2$ nanocomposites [28]. The increase in forward bias current has been observed for p-PANI/n-CdTe and [29] in which barrier height was changed due to the exposure to LPG. They have
reported maximum gas response of 55% for p-PPY/n-TiO₂ heterojunction at 1040 ppm LPG. Comparably, n-CdS/p-PbS NHJ have shown higher gas (60%) response at low gas concentration (1200 ppm).

The response transient curve for first two exposures to LPG is shown in Fig.III.B.7. The experiments carried out at a fixed voltage of 1 V under 1200 ppm of LPG concentration. The n-CdS/p-PbS NHJ demonstrates good reversibility to LPG that has shown maximum response of 60.7%. The response transient curve provides information of response and recovery times of heterojunction. The response time is defined as time at which the current of the heterojunction reaches 90% of the saturation value on exposure of LPG and recovery time is defined as the time required for recovering the 90% of the original current of the heterojunction. Response and recovery times were found to be 102 s and 75 s, for 90% of response and recovery, respectively. The repeatability test for next cycle was performed by exposing sensor to fresh air; and then LPG followed by again fresh air. The test reveals good reversibility with response and recovery times of 72 s and 98 s, respectively. The response and recovery times of the n-CdS/ p-PbS NHJ compared to the PANI based heterojunctions and are tabulated in Table III.1.
Cadmium based n-type semiconductor as a heterojunction partner with p-type inorganic/organic materials towards LPG sensing application

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Heterojunction</th>
<th>Response time (s)</th>
<th>Recovery time (s)</th>
<th>Gas conc. (ppm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>75</td>
<td>1200</td>
<td>Present work</td>
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<td>2</td>
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<td>190</td>
<td>1000</td>
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<td>p-Cu$_2$ZnSnS$_4$/n-ZnO</td>
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<td>p-PANI/n-CdTe</td>
<td>300</td>
<td>600</td>
<td>1820</td>
<td>[29]</td>
</tr>
</tbody>
</table>

Table III.1 Comparison of response and recovery times of n-CdS/p-PbS nanoheterojunction with other heterojunctions compared to the above reports n-CdS/p-PbS nanoheterojunction shown fast response and recovery times with higher gas response value.

Fig. III.B.7 Gas response vs. time (s) of n-CdS/p-PbS nanoheterojunction at fixed voltage of 1V at 1200 ppm of LPG concentration.

III.B.3.3 Stability studies

The stability of the heterojunction is the most important factor for the industrial level manufacturing of the gas sensor device. The stability of the sensor was tested for 10 days at a fixed voltage of 1 V under 1200 ppm of LPG concentration and shown as the variation of gas response against the number of days in fig III.B.8. It is clear that gas response falls 60.7% to 56% (93% of its original value) up to 5 days and remains stable.
Fig.III.B.8 The plot gas response (%) vs. time (no. of days) of n-CdS/p-PbS nanoheterojunction at a fixed voltage of 1V at 1200 ppm of LPG concentration.

III.B.4 Conclusion

The simple, low cost and room temperature chemical method was demonstrated to deposit n-CdS nanowires followed by complete encapsulation with p-PbS nanoparticles to form the nanoheterojunction at room temperature (27 °C). The n-CdS/p-PbS nanoheterojunction was successfully used as liquefied petroleum gas (LPG) sensor at room temperature with the maximum response of 60.7% under exposure of 1200 ppm concentration of LPG at low operating voltage of 1V with low response and recovery times. This study reveals n-CdS/p-PbS nanoheterojunction can be effectively used as room temperature LPG sensor.

All these results are published in Sensors and Actuators B [30].
References


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[23]. JCPDS no. 01-080-1144.


