CHAPTER IV

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

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

IV.A.1 Introduction

Research on nanostructures and their nanoheterojunctions has been rapidly expanding in recent years and very attractive towards electronic applications such as gas sensors [1, 2]. The responses of several nanoheterojunction sensor systems to target gases has been constructed with enhance properties for detection of liquefied petroleum gas (LPG) at room temperature [3]. In recent years, the conducting polymers have been widely investigated as effective materials for room temperature chemical sensors. PEDOT:PSS is commonly accepted to be more environmentally stable than other conducting polymers such as polypyrrole and polyaniline. These features make PEDOT:PSS and its derivatives appealing for gas sensing applications [4]. The Cadmium oxide (CdO), a II-VI group, is an important n-type semiconducting material with direct band gap of 2.5 eV and indirect band gap 1.98 eV [5]. CdO is most promising semiconducting material for different applications such as in solar cells, phototransistors, catalysts and gas sensors [6].

In the present investigation, effort has been taken for the synthesis of necklace like nanostructure of inorganic n-type semiconducting material CdO and formation of a nanoheterojunction by deposition of organic p-PEDOT: PSS on n-CdO nanonecklace so as to provide enough space to adsorption and desorption of gas molecules through highly porous network. The very low cost and room temperature chemical route was used for the synthesis of the nanoheterojunction films on fluorine doped tin oxide (FTO) coated glass substrates. The nanoheterojunction was tested to sense the LPG at room temperature.

IV.A.2 Experimental

For the synthesis of CdO, Cd(OH)$_2$ was synthesized and then air annealed the films to form CdO. For this, the synthesis of Cd(OH)$_2$ nanowires was done by using cadmium chloride (CdCl$_2$) and ammonia as a complexing agent. All the chemicals used, were from Loba chemicals (GR grade) and used as supplied. The commercially available PEDOT: PSS was purchased from Bayer AG. Baytron HC Starck’s and used in optimized proportion with ionized water.

IV.A.2.a Substrate cleaning

The fluorine doped tin oxide (FTO) coated glass substrates were cleaned by the procedure as described in III.A.2.a.
IV.A.2.b Synthesis of CdO necklace like nanostructure on FTO

Initially, Cd(OH)$_2$ nanowires were synthesized at room temperature ($27^\circ$C) by using chemical method reported earlier [7]. Specifically, 0.1 M/L (50 mL) CdCl$_2$ was complexed by drop wise addition of ammonia (10 mL) to the solution. The pH of the complexed bath was maintained at 12. The solution was stirred for few seconds and gently immersed the well cleaned FTO coated glass substrates vertically in a solution along the wall of the beaker at room temperature. After 21 h, the white Cd(OH)$_2$ film was deposited on the substrate surface. Then, substrate was taken out from the solution, rinsed with double distilled water and dried in dry air [8].

Further, Cd(OH)$_2$ film consisting of nanowires was used as precursor for CdO film. CdO necklace like nanostructures was obtained by annealing Cd(OH)$_2$ film at optimized temperature of 290 $^\circ$C in contact with air for two hours. The CdO films were characterized by using XRD, SEM, EDAX and FTIR etc.

**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 ($k_{sp}$) of $[\text{Cd}^{2+}][\text{OH}^2^-]$ is greater than the solubility product ($k_{sp}$) value of Cd(OH)$_2$ ($2\times10^{-14}$) at room temperature. Since hydrated cadmium ion complexes were transferred to cadmium hydroxide through the stepwise replacement of water molecules.

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

The CdO films were obtained by annealing the Cd (OH)$_2$ films at 290 $^\circ$C for 2 hours in air ambient.

$$\text{Cd(OH)}_2 \xrightarrow{290^\circ\text{C}} \text{CdO} + \text{H}_2\text{O} \uparrow$$  \hspace{1cm} (2)

Virtually there is no role of oxygen gas in annealing chamber as reaction itself shows that conversion of Cd(OH)$_2$ takes place by removal of hydroxyl ions. However, we provides air medium during calcinations to maintain the proper stichometry. From this process, whitish Cd(OH)$_2$ films were changed to brown CdO films with the formation of necklace like nanostructure.

IV.A.2.c Deposition of PEDOT: PSS on CdO necklace like nanostructure

The deposition of PEDOT: PSS on CdO nanostructure 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. Different ratios of
PEDOT: PSS::H₂O was used and the ratio 1:4 was found to be optimal. For this, PEDOT: PSS containing 80% water was coated on FTO/CdO film by using dip coating technique. At each time, each volume of PEDOT:PSS::H₂O was ultrasonicated for 1 h. For a single dip, FTO/CdO film was dipped vertically into PEDOT:PSS: H₂O solution for 2-3 seconds and taken out vertically. After 4 to 5 such dips in the intervals of few seconds, a very thin, homogeneous layer of PEDOT: PSS was coated on CdO. The dip coated film of FTO/CdO/PEDOT: PSS was heated at 100 °C for 10 min in air. The PEDOT:PSS::H₂O ratio, ultrasonication, dipping and heating times were optimized with respect to get uniform and thin layer coating of PEDOT:PSS on CdO necklace like nanostructure towards better gas sensing performance.

IV.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 spectrometer (EDAX) attached to the SEM unit. 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 2 V by adopting the same method which was reported earlier.

IV.A.3 Result and discussions

IV.A.3.a Surface morphological and compositional studies

The surface morphology of necklace like CdO nanostructure film under different magnifications are as shown fig.IV.A.1(a) and (b) for 1 µm and 500 nm respectively where as fig.IV.A.1(c) and (d) for PEDOT:PSS coated CdO necklace like nanostructure with magnifications of 1 µm and 500 nm, respectively. From fig.IV.A.1 (a), it clearly shows the string of small beads connected to each other to form necklace like nanostructures. With higher magnification (500 nm), the random distribution of CdO nanonecklace spread on FTO substrate with enough porous surface area is observed (fig.IV.A.1 (b)). It is quite difficult to observe coating of PEDOT:PSS on CdO, rather blurred image gives prediction about the coating of polymer. The lower magnification image clearly depicts the formation of blurred CdO necklace like nanostructure confirming uniform coating of PEDOT: PSS over the CdO necklace nanostructure (fig.IV.A.1(c)). At higher magnification, it is observed that PEDOT: PSS slurry was uniformly coated on CdO to form encapsulation (fig.IV.A.1 (d)). At
the junction between necklaces, PEDOT:PSS stacked to form the bigger particles due to agglomeration, which clearly visualized in lower as well as higher magnification images. The uniform growth of p-type polymer on the n-type necklace like nanostructure results into the formation of high surface area p–n junction at the nano level and hence, the formation of nanoheterojunction. Such unique and novel morphology provides high surface area nano network allowing enough space to adsorb and de-adsorb gas molecules easily at the interface which can finds application as a gas sensor.

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

Energy-dispersive X-ray spectrum of CdO nanonecklace and CdO/PEDOT: PSS on FTO is as shown in fig.A.2. The intensity of generated X-ray is related to the concentration fraction of each element present in the target material. Comparing elemental spectrum of bare CdO (fig.IV.A.2 (a)) with PEDOT: PSS coated CdO
nanonecklace (fig.IV.A.2 (b)), existence of Cd and O peak are observed which confirms the formation CdO. The presence of carbon (0.3 keV) and sulfur (2.3 keV) in the PEDOT:PSS coated CdO nanostructure gives rough confirmation towards the existence of PEDOT:PSS layer on CdO. The appearance of Sn and Si 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. The intensity of Sn peak diminished in PEDOT:PSS coated CdO nanostructure, which supports coating of polymer layer on CdO.

![Fig.IV.A.2 Elemental analysis of (a) FTO/CdO, (b) FTO/CdO/PEDOT:PSS](image)

**IV.A.3.b Fourier transform infrared studies of CdO and PEDOT:PSS coated CdO**

Fig.IV.A.3 (a) shows the FT-IR spectrum of CdO necklace type nanostructure. The peak at 1437 cm\(^{-1}\) attributed to C-C stretching of aromatics. The peaks at 854 cm\(^{-1}\) and 640 cm\(^{-1}\) may be attributed to C-Cl and C-Br stretching of alkyl halides respectively. Inclusion of Cl-group is from used cadmium chloride as a source material. The FT-IR spectrum of PEDOT:PSS coated on CdO nanostructure is as shown in fig.IV.3 (b). The aromatic band due to extended resonance of the polar characteristic related to C=C double bond stretching at about 1641.28 cm\(^{-1}\) in five member vinyl ether group assigned to thiophene ring. The band at 1199 cm\(^{-1}\) occurs due to the C-O stretching. The small peak at 1043 cm\(^{-1}\) may be due to symmetric stretching of S=O [9, 10].
**Fig.IV.A.3.** The FTIR patterns of (a) CdO nanonecklace, (b) PEDOT:PSS coated CdO necklace like nanostructure.

**IV.A.3.c LPG detection at CdO/PEDOT: PSS nanoheterojunction**

The CdO nanostructure and PEDOT:PSS show unintentionally doped n and p-type conductivities, respectively [11, 12]. Fig.IV.A.4 shows the forward biased current density–voltage (J–V) characteristics of the n-CdO/p-PEDOT:PSS nanoheterojunction in air and under various concentrations of LPG (294–1470 ppm). The current density–voltage (J–V) curves between the p-PEDOT:PSS and n-CdO necklace type nanostructure suggest the formation of p–n junction due to formation of thiophene on CdO nanostructure. 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 change in current-densities under different LPG concentrations with respect to air, clearly demonstrates the sensing behavior of the formed nanoheterojunction. As the junction was exposed to LPG, the forward current density was increased up to certain limit. From J–V characteristics, the maximum change in the current-density was observed at 882 ppm concentration of LPG as compared to air, under the bias voltage of 2 V. With further increase in gas concentration to 1470 ppm, the decrease in the current-density was observed. Under different LPG environments, as compared with air, the maximum change in current density was
observed at applied voltage of 2 V. At this voltage, the gas response (S) was calculated using the relation.

\[
S \% = \frac{J_g - J_a}{J_a} \times 100 = \frac{\Delta J}{J_a} \times 100 \tag{3}
\]

where, \( J_a \) is current–density in air and \( J_g \) is current – density in gas environment.

![Forward biased J–V characteristics of FTO/n-CdO/p-PEDOT:PSS necklace like heterojunction in (a) air, and at various concentrations of LPG as (b) 294 ppm, (c) 588 ppm, (d) 882 ppm, (e) 1170 ppm, and (f) 1470 ppm.](image)

Fig.IV.A.4. Forward biased J–V characteristics of FTO/n-CdO/p-PEDOT:PSS necklace like heterojunction in (a) air, and at various concentrations of LPG as (b) 294 ppm, (c) 588 ppm, (d) 882 ppm, (e) 1170 ppm, and (f) 1470 ppm.

The variation of the gas response of the n-CdO/p-PEDOT:PSS heterojunction at various concentrations of LPG at an applied voltage of 2 V is as shown in fig.IV.A.5. The gas response increases from 20.70% to 50.21% with change in LPG concentration from 294 ppm to 882 ppm. The maximum response of 50.21% was observed at 882 ppm of LPG due to the single and complete 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. With further increase in the gas concentration above 882 ppm, a decrease in response (\( S = 39.35\% ; \) 1470 ppm) value was observed. This may be due to saturation of LPG molecules 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.
Cadmium based n-type semiconductor as a heterojunction partner with p-type inorganic/organic materials towards LPG sensing application

Fig.IV.A.5. shows variation in gas response (%) vs. LPG concentration (ppm) of n-CdO/p-PEDOT:PSS nanonecklace like heterojunction at 2 V.

The response transient curves for first two LPG exposures to sensor at fixed voltage of 2 V with 882 ppm concentration of LPG is as shown in fig.IV.A.6. When sensor was exposed to LPG, the sensor reaches the maximum response of 50.21% with response time 163 s. When sensor was exposed to fresh air, removal of LPG molecules shows recovery of the sensor with recovery time 141 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 thus the reason of detachment of gas molecules. 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 177 s and 176 s, respectively.

For industrial applications, the stability study of the nanoheterojunction is very important for manufacturing the gas sensor device. The stability study for n-CdO/p-PEDOT:PSS necklace like heterojunction was carried out over 9 days. The variation of gas response against the number of days is as shown in fig.IV.A.7. It is clear that
Cadmium based n-type semiconductor as a heterojunction partner with p-type inorganic/organic materials towards LPG sensing application.

gas response falls to 45.87 % value up to 6 days and remains stable even after 6 to 9 days showing 91.35 % stability.

**Fig.IV.A.6** Gas response vs. time (s) of n-CdO/p-PEDOT: PSS necklace like heterojunction at fixed voltage of 2V at 882 ppm of LPG concentration.

**Fig.IV.A.7** The gas response (%) vs. time (no. of days) of n-CdO/p- PEDOT :PSS nanoheterojunction at a fixed voltage of 2V at 882 ppm of LPG concentration.
IV.A.3.d LPG sensing mechanism of n-CdO/p-PEDOT:PSS nanoheterojunction

The two different semiconducting materials having different band energies with their electron affinities and work functions form hetero-junction. Band gap energy and electron affinity are fundamental properties of material, whereas work function changes as per doping level and ultimately depend on the position of Fermi level [13].

The use of FTO below CdO layer and use of Ag on top of PEDOT:PSS forms good ohmic contacts. The difference in band energies of p-PEDOT:PSS and n-CdO, forms a barrier at the interface, which form p-n junction diode like characteristics, leads to flow of charges in forward bias situation. Sharma et al. showed barrier formation between PEDOT:PSS and ZnO [14]. The schematic presentation of energy band diagram is as shown in fig.IV.A.8.

![Band diagram of n-CdO/p-PEDOT:PSS nanoheterojunction](image)

The electrical characteristics of n-CdO/p-PEDOT:PSS nanoheterojunction are affected by the exposure to liquefied petroleum gas (LPG) at interface. The forward bias current-voltage (J-V) characteristics shows, the change in conductivity upon exposure of LPG as compared to air environment. The gas response increase from 20.70% to 50.21% with increase in LPG concentration from 294 ppm to 882 ppm and attained maximum value at 882 ppm. As PEDOT:PSS layer is highly porous, the LPG molecules are adsorbed preferentially on PEDOT:PSS and interacts at the junction interface. The adsorption of LPG at PEDOT:PSS surface donates electrons, as a result the carrier concentration of nanoheterojunction changes, resulting in decrease in the
barrier height, which leads to decrease in resistance and thus, increase in current density value [15]. This leads to change in electron affinity of p-PEDOT:PSS and caused into change in barrier height of junction [16-20]. Hence, gas response value was enhanced because gas response is a function of gas concentration, which is due to change in barrier height of the potential barrier. Above 882 ppm of LPG concentration, the response value decreased drastically since the effect of active area was diminishing due to layer by layer formation and thereby saturation of heavier density of gas molecules at the interface [21].

**IV.A.4 Conclusions**

In present work, we have successfully synthesized necklace like nanostructure of n-CdO onto FTO coated glass substrates by simple and low cost chemical method followed by deposition of p-PEDOT:PSS on n-CdO by simple dipping technique. Formation of such a novel morphology of n-CdO/p-PEDOT:PSS necklace type nanoheterojunction with high surface area leads to demonstrate a liquefied petroleum gas (LPG) sensor with gas response of 50.21% under the exposure of LPG (882 ppm) at room temperature (27 °C). The device showed low values of response and recovery times. The device showed decrease in response value up to 8.65 % of its original value 50.21% i.e. 91.35% stability value after six days and remains stable thereafter. The gas sensing properties indicates that n-CdO/p-PEDOT:PSS nanoheterojunction thin film was an excellent candidate for LPG detection at room temperature.

**IV.B Synthesis and characterization of n-CdO/p-PbS nanoheterojunction and its application as a LPG sensor**

**IV.B.1 Introduction**

Present investigation focuses on the synthesis of Cd(OH)$_2$ nanowires by using simple low cost wet chemical route method at room temperature on to FTO substrates and their conversion to CdO necklace like nanostructures by optimized thermal treatment. Thereafter, p-PbS nanoparticles on n-CdO necklace like nanostructure were deposited to form n-CdO/p-PbS nanoheterojunction thin film for the detection of LPG sensing at room temperature (27 °C).

**IV.B.2 Experimental**

The synthesis of CdO, was done by air annealing of Cd(OH)$_2$ films to form CdO. For this, the synthesis of Cd(OH)$_2$ nanowires was done by using cadmium
chloride (CdCl\(_2\)) and ammonia as a complexing agent. The deposition of PbS on CdO was done by using lead nitrate [Pb(NO\(_3\)]\(_3\)] and sodium sulphide [Na\(_2\)S] as cationic and anionic precursors, respectively. All the chemicals used were from Loba chemicals (GR grade) and used as supplied.

**IV.B.2.a Synthesis of CdO necklace like nanostructure on FTO**

Substrate cleaning and synthesis of necklace type nanostructures of Cadmium Oxide (CdO) onto fluorine doped tin oxide (FTO) coated glass substrates is same as described in Chapter IV.A.2.a and IV.A.2.b, respectively.

**IV.B.2.b Synthesis of PbS nanoparticles onto CdO necklace like nanostructure**

The successive ionic layer adsorption and reaction (SILAR) method was employed to deposit PbS nanoparticles onto CdO nanonecklace at room temperature (27 °C). Lead nitrate [(PbNO\(_3\)]\(_3\)] with concentration 8 mM/L was used as a cationic precursor at pH of 9 and 5 mM sodium sulphide (Na\(_2\)S) solution was used as an anionic precursor at pH of 11. The immersion time in anionic and cationic precursors was 20 seconds with rinsing time of 10 seconds in double distilled water. The immersion cycles were optimized to get the complete coverage of PbS nanoparticles onto CdO necklace like nanostructure to form better nanoheterojunction towards enhanced gas sensing performance [22].

**IV.B.2.c Characterization techniques**

The structural properties of the films were studied by using X-ray diffractometer (XRD)(D8 Advance, Bruker) whereas surface morphology was viewed by high resolution field emission scanning electron microscopy (FE-SEM, JEOL 6360A), attached with energy-dispersive X-ray spectrometer (EDAX). The gas sensing properties of n-CdO/p-PbS were studied on the home made gas sensor unit, under forward biased current density–voltage (J–V) characteristics between 0 and 2 V.

**IV.B.3 Results and discussion**

**IV.B.3.a Structural studies**

Here, the CdO nanonecklace were obtained simply by calcinations of the Cd(OH)\(_2\) nanowires at 290 °C in air for two hours. Fig.IV.B.1 (a) shows X-ray diffraction (XRD) patterns of CdO sample. The peaks marked by stars are due to contribution from FTO substrates. All the peaks corresponding to (111), (200), (220), (311), and (222) planes confirms pure cubic phase with space group Fm\(_3m\) (225) and measured lattice constant of a = 4.73 Å [23]. Fig.IV.B.1 (b) shows XRD pattern of
PbS deposited on CdO films. Peaks corresponding to (006), (008), (116), (204), and (422) gives better support for the formation of PbS nanoparticles on CdO nanonecklace [24] whereas (111), (200), (220), (222), and (311) supports the existence of CdO material below PbS nanoparticles.

**Fig.IV.B.1** the XRD patterns of (a) FTO/CdO (b) FTO/CdO/PbS

**IV.B.3.b Surface morphological studies and elemental analysis**

The SEM images of Cd(OH)$_2$, CdO and CdO/PbS thin films are as shown in Fig.IV.B.2 (a), (b) and (c), respectively. The formation of Cd(OH)$_2$ nanowires is as shown in Fig.2 (a). Fig.2 (b) clearly shows the formation of novel necklace type nanostructure of CdO, with interconnected small beads to form necklace like structure. From Fig.IV.B.2 (b), it is observed that PbS particles were coated on surface of CdO necklace like nanostructure to form heterojuction. The uniform deposition of p-type PbS on the n-type CdO necklace like nanostructure results into the formation of high surface area p–n junction at the nano level and hence, the formation of nanoheterojunction.
The energy-dispersive X-ray spectrum (EDAX) of CdO and CdO/PbS nanonecklace on FTO substrates are as shown in Fig.IV.B.3(a-b). The elemental analysis confirms the formation of CdO on FTO (Fig.IV.B.3(a)) due to presence of Cd, and O peaks. The inclusion of Sn and Si is from FTO and glass substrate whereas presence of Au is from coating of Au on sample. The elemental analysis confirms formation of PbS on CdO nanostructures on FTO due to presence of Cd, O, Pb and S peaks (Fig.IV.B.3(b)). EDAX results supports well with XRD results.

Fig.IV.B.2 SEM images of (a) Cd(OH)$_2$ (b) CdO (c) CdO/PbS on FTO with scale bar 500 nm.

Fig.IV.B.3. EDAX of (a) CdO (b) PbS deposited CdO necklace like nanostructure

IV.B.3.c LPG sensing properties of n-CdO/p-PbS nanoheterojunction

The heterojunction formed between CdO and PbS was tested by coating Ag paste on PbS layer. The complete device FTO/n-CdO/p-PbS/Ag layer is designed and current density – voltage (J-V) curves for the devices were tested. The forward biased current density–voltage (J–V) characteristics of the n-CdO/p-PbS nanoheterojunction in air and under various concentrations of LPG is as shown in fig.IV.B.4. The formed
Cadmium based n-type semiconductor as a heterojunction partner with p-type inorganic/organic materials towards LPG sensing application

n-CdO/p-PbS NHJ was tested as a sensor towards liquefied petroleum gas (LPG) at room temperature (27 °C). The current density of heterojunction in air \((J_a)\) and in the presence of LPG \((J_g)\) were measured at a fixed voltage and following equation was used to calculate the gas response.

\[
S\% = \frac{J_g - J_a}{J_a} \times 100 = \frac{\Delta J}{J_a} \times 100
\]

Fig.IV.B.4 (a) depicts J-V characteristics of n-CdS/p-PbS nanoheterojunction in air as a reference and under the various concentrations of LPG from 294 – 1470 ppm (Fig.IV.B.4 (b-f)). After exposure of LPG towards the junction, the forward current density enhances with LPG concentration. The maximum change in the current density was observed for 1176 ppm concentration of LPG at 2 V.

![J-V characteristics](image)

**Fig.IV.B.4** J-V characteristics in (a) air, and (b) 274 ppm (c) 588 ppm (d) 882 ppm (e) 1176 ppm (f) 1470 ppm concentration of LPG

The gas response at various concentrations of LPG was calculated at a fixed voltage of 2V and is shown in Fig.IV.B.5. The gas response increases from 11.76 % to 51.10 % with increase in LPG concentration and attained maximum 51.10 % at 1176 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 1176 ppm, a decrease in response value was observed at 1470 ppm which may be due to formation of multilayer of gas molecules at the interface of the junction; the potential barrier height may increases at the interface or may be due to recombination of charge carriers.

![Image: Gas response at various concentrations of LPG at a fixed voltage 2 V](image)

**Fig.IV.B.5** Gas response at various concentrations of LPG at a fixed voltage 2 V

The response transient curves for first two exposures to LPG at fixed voltage of 2 V and 1176 ppm of LPG are as shown in Fig.IV.B.6. The n-CdO/p-PbS heterojunction shows good reversibility to LPG that has shown maximum response of 51.10%. The response transient curve provides information of response and recovery times of heterojunction. Upon exposure to LPG, the sensor reaches the maximum response of 51.10% with response time 150 s. Further when sensor exposed to fresh air, sensor shows recovery time 134 s. 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 148 s and 142 s, respectively.
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Fig.IV.B.6. Gas response vs. time (s) of n-CdO/p-PbS necklace like heterojunction at fixed voltage of 2V at 1176 ppm of LPG concentration

Fig.IV.B.7 The plot of gas response (%) vs. time (no. of days) of n-CdO/p-PbS necklace like heterojunction at a fixed voltage of 2V at 1176 ppm of LPG concentration.

The stability study of nanoheterojunction is very important in order to design and manufacture the long term stable gas sensor device for domestic as well as industrial applications. The stability study for n-CdO/p-PbS nanonecklace like
heterojunction was carried out over 8 days. Fig.IV.B.7 shows the variation of gas response against the number of days. It is clear that gas response falls from 51.10 % to 48.31 % that means response value decreases up to 2.79 % of its maximum value (51.10 %) in 6 days and remains stable even after 8 days which shows 94.54 % stability.

IV.B.3.d LPG sensing mechanism of n-CdO/p-PbS nanoheterojunction

When n-CdO/p-PbS heterojunction is exposed to LPG, due to reducing nature of the interacting species, the resistance of nanoheterojunction decreases and gas response is increased as LPG concentration goes on increasing. At higher concentration of LPG, the response may decreases due to saturation of LPG molecules at the junction. The sensing property of sensor to reducing gas LPG, may relates surface chemical oxygen absorption of sample, also the role of chemisorptions or atmospheric oxygen adsorbs on the surface by extracting electrons from sensing material, this makes reduction of barrier height, leading to decrease in resistance and increase in gas response. The fig.8 shows schematic representation band diagram of n-CdS/p-PbS nanoheterojunction. Alternatively, upon exposure to LPG, it likely seems to be dissociation of reducing gas LPG at surface or interface of the junction. This leads to change in work function of p-PbS and increases the carrier concentration near the interface of nanoheterojunction. Hence in turn barrier height of the nanoheterojunction decreases. The change in potential barrier height and depletion width at the heterojunction interface is responsible for current transporting through the nanoheterojunction [25-35].

![Band diagram of n-CdO/p-PbS nano heterojunction](image)

**Fig.IV.B.8** Band diagram of n-CdO/p-PbS nano heterojunction
IV.B.4 Conclusion

Necklace like nanostructure of CdO was obtained by annealing Cd(OH)$_2$ nanowire film at optimized temperature 290 °C for two hours in air. It shows the string of small beads connected to each other to form necklace like structure. Such nanostructures having unique surface morphology may be potential candidates for gas sensing device. The p-PbS was successfully deposited by successive ionic layer adsorption and reaction (SILAR) method on to n-CdO nanonecklace to form n-CdO/p-PbS nanoheterojunction at room temperature (27 °C). The n-CdO/p-PbS nanoheterojunction was successfully used as liquefied petroleum gas (LPG) sensor at room temperature (27 °C) with the maximum response of 51.10% under exposure of 1176 ppm concentration of LPG at operating voltage of 2V with low response and recovery times.
References

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