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Synthesis, Characterization and Study of H_2S Gas Sensing Properties of CdO Doped in Nanocrystalline Pollyaniline

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Abstract: ***Polyaniline PANI and CdO/ PANI nano composites were synthesized by in situ polymerization technique and characterized by Fourier transform infrared spectra (FTIR), X-Ray diffractometer (XRD), Field Emission Gun Scanning Electron Microscopy (FEG SEM), which confirms the presence of CdO in PANI matrix. The synthesized materials were further used for sensing various gases like LPG, NH_3, CO_2 and H_2S gas. The change in resistant of the material with time was recorded after the response of H_2S gas. The increase in electrical resistance is due to transfer of charge from sensing material to analyse gas and absorption of gas into the polymer matrix. The sensitivity was found maximum for H_2S. The 50 wt% CdO/PANI nano composite showed maximum sensitivity (300%) for 400ppm of H_2S gas***

Keywords: Conductive polymer, Polyaniline based nonocomposite, CdO nanorods, chemical synthesis, H_2S gas sensor, Time response.

1. Introduction

Hydrogen Sulphide is a colorless, flammable, extremely hazardous gas with a "rotten egg" smell. It occurs naturally in crude petroleum and natural gas, and can be produced by the breakdown of organic matter and human/ animal wastes (e.g., sewage). It is heavier than air and can collect in low-lying and enclosed, poorly ventilated areas such as basements, manholes, sewer lines and underground telephone/electrical vaults.

A gas sensor is a device which detects the presence of different gases in an area, especially those gases which might be harmful to humans and animals. There is a high demand for small and low cost gas sensors for indoor and outdoor air quality monitoring, medical diagnosis and control of food quality or safety of industrial process. The development of gas sensor technology has received considerable attention in recent years for monitoring environmental pollution. It is well known that chemical gas sensor performance features such as sensitivity, selectivity, time response; stability, durability reproducibility and reversibility are largely influenced by the properties of the sensing materials used.

Many kinds of materials such as conducting polymers [1], semiconductors have been used as a sensing material to detect the targeted gases based on various sensing techniques and principles. Conducting polymers are chosen for gas sensing due to several advantages such as their low operating temperature of 0^0C to 60^0C and low cost. Various techniques were explored for the synthesis of Poly Aniline from its monomer Aniline. [2] Formation of mixed phases of polymer together with conducting emeraldine salt phase is confirmed from the spectroscopic techniques. The temperature dependant electrical resistance measurements show thermal activated exponential behaviour. [3]-[5]

Polyaniline received great attention in gas sensor due to their short response in time, simple method of synthesis, easy modification of their molecular chain structure and high sensitivity at room temperature. Early work explains polyaniline sensing mechanism based on changes in their conductivity when they are exposed to certain gases due to doping or dedoping process. Conducting polymer such as PANI is well known to be sensitive to ammonia, CO, methanol, NO_2, LPG [6]-[10].

Polymer-based sensors have several advantages for gas detection. Polyaniline (PANI) [11] is a promising material because of its intrinsic electrical conductivity by doping with organic dopants.

PANI is unique as its electronic properties [12] can be controlled both by varying the oxidation state of the main chain and conductivity can be enhanced in several orders of magnitude for the condition by doping it with different materials.

In recent years, many researchers have focused on cadmium oxide (CdO) due to their applications in several areas of research, specifically in optoelectronic and other applications, Reduction in the dimensionality of such materials from the three dimensional bulk phases to the zero-dimensional nanoparticles can lead to enhanced non-linearity, determined by the quantum size effects Because of these interesting possibilities, there has been some effort to prepare nanoparticles of CdO. [13]-[14]

Appropriate addition of nano particulates or nanoscale fillers [15] to the polymer matrix and good dispersion of these fillers not only enhances its performance but also introduces new physical properties and novel behavior to the original polymer matrix.

In earlier work, it was reported that the significant enhancement is observed when TiO_2 nanoparticles are incorporated in polyaniline compared to earlier work. The 30 wt.% of PANI/TiO_2 nanocomposites at 400 ppm shows the maximum sensing response for LPG of about 90%. The results obtained for these nanocomposites are of scientific and technological interest [16]. Roy [17] studied the sensing parameters and electrical properties of CdO/PANI nano composite. He observed that 75% of sensitivity for 400 ppm of LPG.

In present context, cadmium oxide nanoparticles are embedded in the polymer matrix. Appropriate addition of nano particulates to the polyaniline matrix and good dispersion of these fillers not only enhanc its performance but also introduces new physical properties and novel behaviour to the original polymer matrix. It is also observed that electrical conductivity of polyaniline vary as the concentration of the filler for nano particles varies. The synthesized CdO/PANI nanocomposites were further characterized with FTIR, XRD, FESEM and electrical conductivity studies. Also the sensing parameters were studied for various gases like LPG, NH_3, CO_2 and H_2S gas.

2. Experimental Details

The monomer aniline (RANKEM) was doubly distilled prior to use. Ammonium persulphate ($(NH_4)_2S_2O_8$) (Fisher Scientific), Hydrochloric acid (HCl) (RANKEM), Cadmium oxide (CdO), were procured and used as received.

Fig. 1 is a schematic representation of synthesis of CdO/PANI nanocomposites, In this work, synthesis of CdO/PANI nanocomposites was done by *in situ* polymerization. The 0.1 M of aniline was dissolved in 1 M HCl [used as a protonic acid] and stirred for 10 minutes to get aniline hydrochloride. To this solution, 0.1 M of Ammonium persulphate (which acts as oxidant was added drop wise with continuous starring for 1 hr at 0-5^{0}C to polymerize. Fine graded powder of Cadmium oxide (CdO) was varied in weight percentages (10, 20, 30, 40 and 50) and added to polyaniline solution with vigorous stirring in order to keep the CdO suspended in the solution. This reaction mixture was stirred for 3 hr at 0-5 ^{0}C with magnetic stirrer in order to disperse CdO in the polymer solution. The suspension was left for 20 Hr for polymerization. Finally, the suspension was filtered and washed with distilled water repeatedly and dried under vacuum at 60^{0}C for 8 hr. The obtained nanocomposites were crushed into fine powder in an agate mortar.

The sequence of coloration is

light blue → blue green → coppery tint → green precipitates

The pellets of 13 mm diameter are formed with thickness varying up to 2 mm by applying pressure 6 ton using pallet maker. For sensor studies, the copper electrodes are placed on each of the surface of pellets to obtain better ohmic contact.

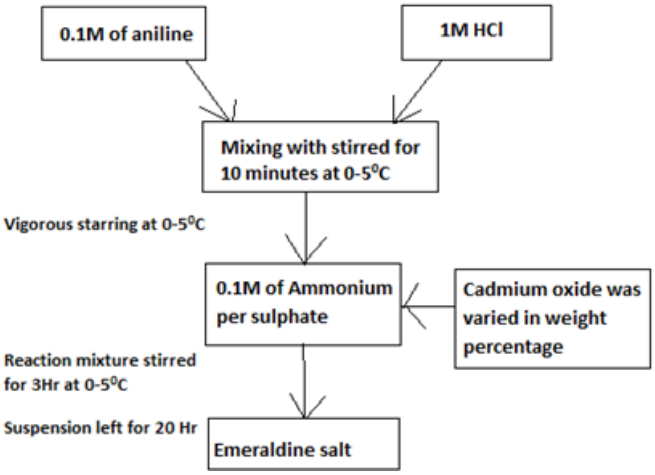


Figure 1: Flowchart showing the various steps involved in synthesis of CdO-PANI

3. Characterization

X-ray diffraction (XRD) analysis of the synthesized nanocomposites was conducted on advanced X-ray Difffractometer (Bruker, Karlsruhe, Germany) with CuK α1 radiation ($\lambda = 1.5404^0$A within the 2θ range of 20-80^0. Actual morphology of as prepared nano-material have been judged using Fe-SEM (Hitachi S-4800, Japan, 1.4nm, 800kV). Nova Nano FEG-SEM 450 with EDAX (Mapping System) facility to study sample size, shape, surface features at nano scale level along with elemental analysis. For measurement of voltage, current, resistance of pellet programmable 4 ½ Digital Multimeter SM5015 along with homemade gas sensing unit used shown in fig. 2 (a). The suspension was dried under vacuum at 60^{0}C in homemade oven as shown in fig. 2 (b).

(a) (b)

Figure 2: Photograph of the (a) gas sensor setup (b) oven

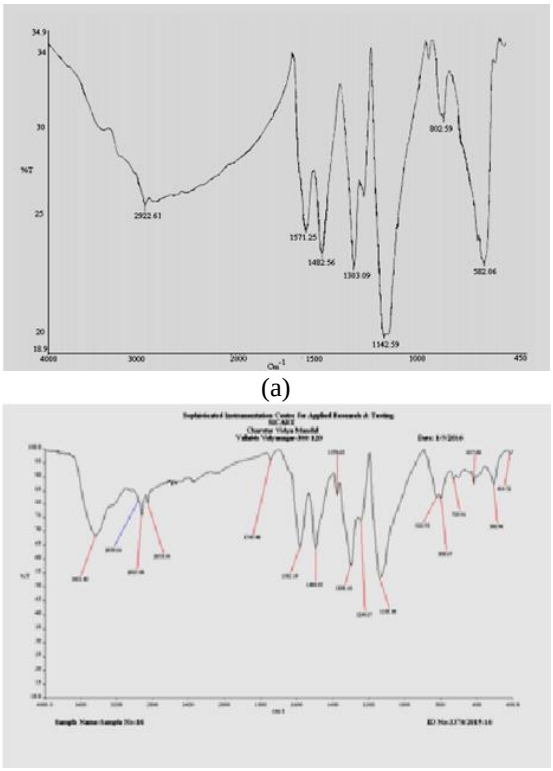
2.1 FT-IR analysis

Careful analysis of the FTIR spectra of pure polaniline reveals the presence of intensity peaks at 3428 cm^{-1} for N-H stretching, 2924 cm^{-1} for C-H stretching, 1293 cm^{-1} for C-N stretching + C-H bending, 1239 cm^{-1} for C-N stretching + C-C stretching, 794 cm^{-1} for deformational C-H (out of plane) of 1-4 di-substituted aromatic ring (Benzenoid). The characteristic peaks appear at 1563 cm^{-1} and 1485 cm^{-1} which corresponds to C= C stretching of quinoid rings and stretching of the benzenoid ring respectively, confirms the formation of polyaniline. [18]

Fig. 3 (a) shows the FTIR spectra for pure Polyaniline. [19] The absorption peaks are found to be at 1561 cm $^{-1}$, 1480 cm^{-1} , 1302 cm $^{-1}$, 1140 cm $^{-1}$ and 801 cm $^{-1}$, corresponding to the C=N stretching of quinoid ring, C-H stretching of

benzoid ring, the C-N stretching of benzenoid ring, the characteristic vibrating mode of quinoid ring and the blending of C-H bond in aromatic ring, respectively.

Fig. 3 (b) shows the FTIR spectra of CdO/PANI composite with 50 wt% CdO in PANI. The characteristic stretching frequencies are observed at 3433.40 cm^{-1} is due to N-H stretching, 2853.58 cm^{-1} 2925.8 cm^{-1}, 2959.01 cm^{-1} are due to C-H stretching, 1745.46 cm^{-1} due to C= O stretching, 1582.19 cm^{-1} due to N-H bending, 1494.95 cm^{-1} due to C-C stretching 1300.16 cm^{-1} , 1244.17 cm^{-1}which conforms the C-N stretching of primary aromatic amines. 1138.36 cm^{-1} reveals the C-H bending vibrations. The absorption bands lies below 1000 cm^{-1} are the characteristics of mono substituted benzene. The same finding has been elsewhere [20]



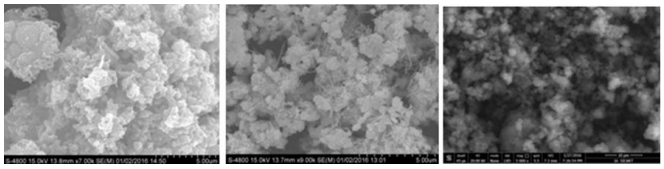
(a)

(b)

Figure 3: FTIR spectra (a) pure PANI (b) PANI/CdO composite (50 wt% CdO in PANI)

2.2 FE-SEM analysis

The FESEM images of PANI, CdO and CdO/PANI nano composites are shown in fig. 4 (a,b,c), All the nanocomposites reveal flaky shaped structure, in which the size of flakes reduces as more percentage of CdO nanorods is added into PANI. It can be seen that the size of final crystals of CdO covered by PANI reduced with increasing CdO nano rods content due to the possibility of an assemblage of CdO particles and PANI has declined. The FESEM images help us draw a conclusion that the doping of CdO nano rods has strong effect on morphology of PANI, since PANI has various structures such as granules, nanofibers and flakes.

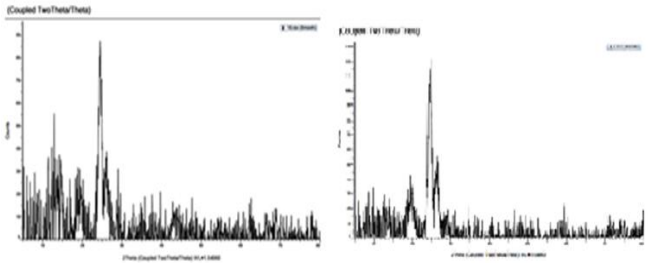


(a) (b) (c)

Figure 4: (a) SEM of pure PANI, (b) SEM of pure CdO, (c) SEM of pure PANI/CdO 50 wt% of Cdo in PANI

2.3 XRD analysis

XRD analysis was used to examine the structure of PANI and PANI-CdO nanocomposite and investigate the effect of the various amounts of CdO nanorods on the PANI structure.



(a) (b)

Figure 5: a) X ray diffraction patterns of pure PANI (b) X ray diffraction patterns of 50 wt% CdO in PANI

Fig. 5 (a) shows the typical XRD patterns of PANI nanocomposites. As is evident in PANI and its nanocomposites broad diffraction picks occur between 10^0 to 30^0 due to the parallel and perpendicular periodicity of the PANI. The PANI peak diffracted at an angle of $2\theta = 20.172^0$ and $2\theta = 24.133^0$ with a d spacing 4.3985^0A and 3.6849^0A, respectively, in the XRD pattern which shows low crystallinity of the conductive polymers.

It can be seen that the XRD patterns of nanocomposites are similar to that of PANI. According to fig. 5 (b) in the given range recorded for the broad peak, two distinct sharp peaks at $2\theta = 24.38^0$ and $2\theta = 44.06^0$ with planes of (111) and (200) respectively, are shifted negligibly but their intensity increases as the content of CdO nanorods in PANI-CdO nanocomposite increased.

4. Electrical Conductivity Measurement

An electrical resistance of the pellets was measured at room temperature using the four-point probe technique. The conductivity σ of the pallet is given by [21]-

$$\sigma = 1/[(\pi/\ln 2)*R*d\ ] \quad (1)$$

where,
$(\pi/\ln 2)*R$ is the sheet resistance
d is the thickness of the pellet.

Fig. 6 shows the variation of current with different voltages was measured by using the four point probe technique. Model keithley. The conductivity σ of the pellet was calculated by using the above equation. In oxidative method, the conductivity of the prepared CdO-PANI nanocomposites pellets is 0.31576 S/cm.

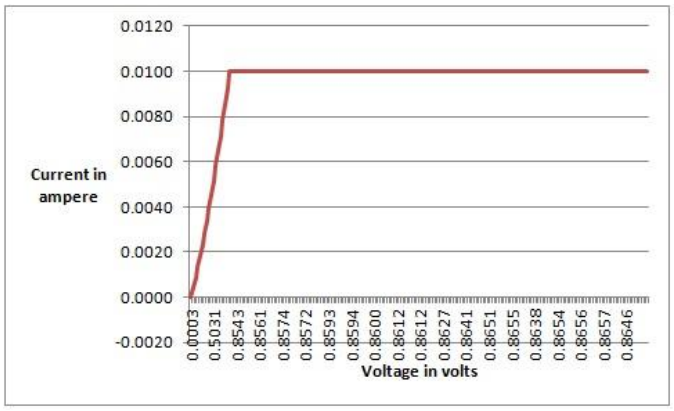


Figure 6: I-V characteristic of 50 wt% CdO in PANI

5. Sensor Response Towards Hydrogen Sulphide

Fig. 7 shows the change in electrical resistance with concentration of H_2S in parts per million at constant volume of pure PANI and CdO/PANI nanocomposites at room temperature (27^0C). It is also observed that among all the CdO/PANI nanocomposites, 40% and 50% nanocomposites shows maximum change in resistance when compared to pure PANI and other nanocomposites of different wt% of CdO in PANI (10, 20, 30 wt%).

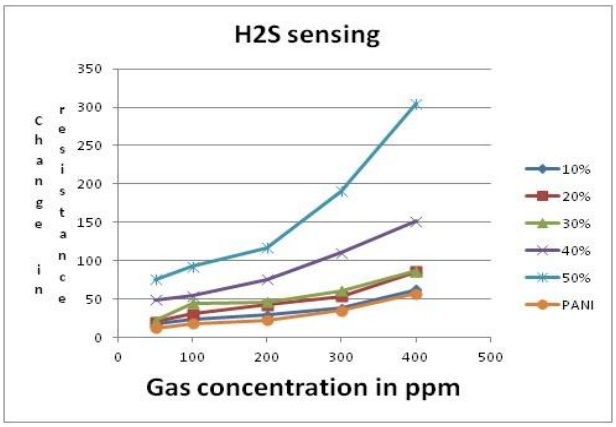


Figure 7: Sensitivity for various test gases at 400 ppm of H_2S gas

Fig. 8 shows the sensitivity against time for CdO/PANI nanocomposites. It is observed that, the sensitivity lies between 150 to 305% at 400ppm for 40 and 50 wt % CdO/PANI nanocomposites whereas for PANI, 10, 20, 30 wt % nanocomposites sensitivity is less than 85%. The response time 16 sec at 400 ppm and recovery time 6 sec at 400 ppm for CdO/PANI 50 wt% nanocomposite. The response in the resistance may be due to the adsorption of gas on the surface of the sensing materials which increase the size of the sensing layer. The increase in volume causes an increase in resistance which disturbs the conductive pathway through the material. When the gas is desorbed the polymer returns to its original size, restoring the conductive path-ways. Thus electrical resistance increases with increase in the concentration of gas.

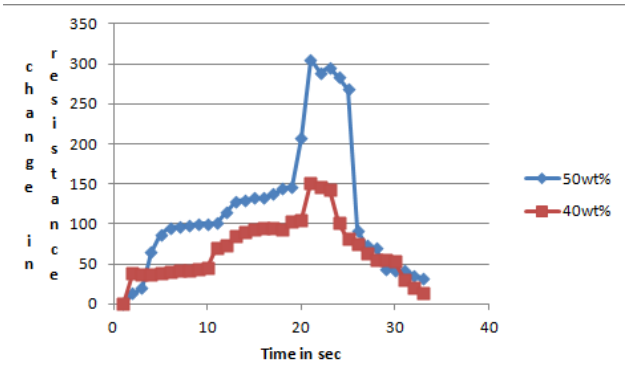


Figure 8: Recovery and response time of 40 and 50 wt% of CdO in PANI

Fig. 9 shows the variation of selectivity of the CdO/PANI nanocomposites for various gases such as H_2S, CO_2, LPG and NH_3. It is observed that the 50% CdO/PANI nanocomposites showed 60% response for CO_2 gas, 75% for LPG, 90% for NH_3 whereas 300% for H_2S gas. The maximum response for H_2S gas may be due to interaction in CdO nanoparticles with H_2S and also due to oxidizing nature. Hence it is one of the promising H_2S sensing materials for device fabrication.

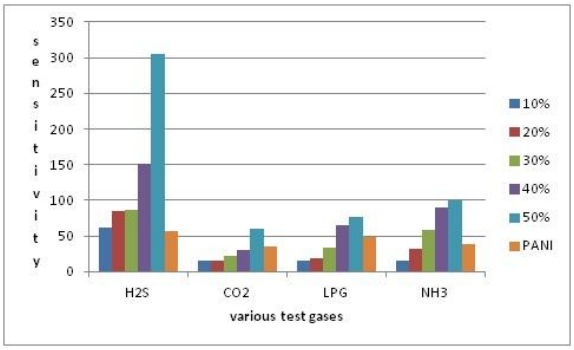


Figure 9: Variation of sensitivity for various gases test gases

6. Conclusion

In this present paper, we have fabricated a CdO/PANI nano composites gas sensor. The nanocomposites were synthesized by in situ polymerization. Formation of mixed phases of polymer together with conducting emeraldine salt phase is confirmed from the spectroscopic techniques. In case of polyaniline and CdO/PANI nanocomposites it is due to both the PANI sensing mechanism of swelling and CdO sensing mechanism of surface charge are responsible for variation of resistance with increase in concentration of gas within the sensing material. The minimum concentration of H_2S that can be determined is 50 ppm. The high sensitivity of about 300 is obtained for 400ppm of H_2S at room temperature.

7. Acknowledgment

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