

Synthesis, Characterization and Comparative Study of NH₃ and H₂S Gas Sensing Properties of PANI/CdO Nanocomposites

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ABSTRACT: Nanocomposites of polyaniline with CdO nanoparticles have been synthesized by in-situ chemical polymerization method the usage of ammonium persulphate (APS) as the oxidant. Nano rods of cadmium oxide (CdO) changed into synthesized the usage of co-precipitate technique. The compositional, surface morphological study of the polymer and the nano composites were characterized by Fourier Transform Infra Red spectra (FTIR), XRD, Transmission Electron Microscopy (TEM), Field Emission Gun Scanning Electron Microscopy (FEG-SEM). The FTIR peaks of PANI had been observed to shift to better wave wide variety in PANI/CdO nano composites because of the formation of H-bonding. X Ray Diffraction pattern revealed that the crystallinity of PANI increases after addition of CdO nano rods, while the intensity of the peaks extended with the aid of the addition of CdO nano rods. The morphology of the nano composites is studied by means of FEG-SEM and TEM evaluation respectively. The synthesized materials were further used for sensing various gases like LPG, NH₃, CO₂ and H₂S gas. The sensing abilities, including sensitivity, response time and recovery time, to various vapour concentrations, ranging from 50 ppm to 400 ppm, were investigated. The change in resistance of the material with time was recorded after the response of H₂S and NH₃ gas. The increase in electrical resistance is due to transfer of charge from the sensing material to the analysed gas and absorption of gas into the polymer matrix.

KEYWORDS: PANI, CdO, FTIR, XRD, TEM, SEM, Gas Sensor.

I. INTRODUCTION

Ammonia (NH₃) and hydrogen sulphide (H₂S) are both gasses of obnoxious, feature odours. Ammonia, in particular at higher concentrations, is a stifling gas inflicting irritation of eyes and the respiration system. Hydrogen sulphide is the primary compound of the "rotten egg" scent. Both gasses are sensed by using the human nostril at very low concentrations. Consequently, their presence within the exhaust gasses from cars operated in enclosed areas is mostly be counted of pain and look rather than a fitness threat. All conditions that favour or enhance the chemical reduction interest of the three-manner catalyst are in all likelihood to growth the formation of NH₃ and H₂S. Those conditions include excessive catalyst temperatures, low exhaust gas space velocities, wealthy, gas combinations [1].

Among organic conducting polymers, polyaniline (PANI) is regarded as one of the most technologically promising conductive polymers because of its intrinsic electrical conductivity by doping other dopants and the monomer is inexpensive, the polymer can be easily prepared by oxidative polymerization with high yield, and products are stable under ambient conditions [2-5]. A small amount of the nano components should improve the overall performance of the polymeric substances. This is attributable to the small size, large particular place, quantum confinement results and the study interfacial interaction of the nano materials. The conductivity of polymers can be tuned by means of several orders of value just as in inorganic semiconductors. This tunable conductivity can be finished through numerous doping mechanisms like 'chemical doping with the aid of charge transfer', 'electrochemical doping', 'photo doping', fee induction at metallic-semiconductor interface' and 'doping by means of acid-base

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chemistry [6]. Polyaniline (PANI) own terrific thermal and environmental stability. Polyaniline has been utilized in an expansion of packages like diodes, sun cells, and in gas sensors. Polyaniline (PANI) is a promising fabric due to its intrinsic electric conductivity through doping with organic dopants [7]. CdO is an n-type semiconductor metallic oxide with a band hole of two.16 eV at room temperature, with a huge band hole, low electric resistivity and excessive transmission inside the seen region due to these residences, it has been broadly investigated in various fields which include photovoltaic cells, transparent electrodes, and so forth [8-10].

In this paper an attempt has been made on synthesis and characterization of PANI and its nano composites with CdO nano rods by way of in-situ oxidative polymerization of aniline monomer with ammonium persulphate (APS). Samples were characterized by means of FTIR spectra, XRD, TEM, FEG-SEM. The interaction between PANI and CdO nano rods turned into investigated and the results exhibit the doping impact of CdO nano rods. The sensing mechanism was also discussed.

II. EXPERIMENTAL PROCEDURE**A. SYNTHESIS OF NANOSTRUCTURED POWDER**

Prior to experiments, the AR grade aniline [S. D. Lab. Mumbai] Ammonium persulphate ((NH₄)₂S₂O₈) [Thermo Fisher Scientific], Hydrochloric acid (HCl) [Rankem], Cadmium oxide (CdO), were procured.

In this work, synthesis of PANI/CdO 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 in drips with continuous stirring for 1 hr at 0 - 5^oC for polymerizing. Fine graded powder of Cadmium oxide (CdO) was varied in weight percentages (10, 20, 30, 40 and 50) and added to the polyaniline solution with vigorous stirring in order to keep the CdO suspended in the solution. This reaction mixture was stirred for 3 hrs at 0 - 5^oC with magnetic stirrer in order to disperse CdO in the polymer solution. The suspension was left for 20 hrs for polymerization. Finally, the suspension was filtered and washed with double distilled water repeatedly and dried in vacuum at 60^oC for 8 hrs. The nano composites thus obtained were crushed into fine powder in an agate mortar.

B. PELLETS FABRICATION

The pellets of 13 mm diameter were formed with thickness varying 1.5 to 2 mm by applying a pressure 8 tons using pellet maker. For sensor studies, the copper electrodes were placed on each of the surface of pellets to obtain a better ohmic contact.

III. MATERIAL CHARACTERIZATION**A. STRUCTURAL PROPERTIES (X-RAY DIFFRACTION STUDIES)**

X ray diffraction study of pure and CdO doped PANI powders was carried out using BRUKER AXSD8 (Germany) advance model X ray diffraction with CuK α_1 ($\lambda=1.54056 \text{ \AA}$) radiation in the 2 θ range 20^o-80^o. The scanning speed of the specimen was maintained 0.5^o/min. Fig. 1 shows the XRD pattern of pure and CdO doped PANI powders. The 2 θ peak observed at 25.09^o, 26.82^o and 72.041^o. The XRD spectrum reveals that the materials are polycrystalline in nature. The observed peaks are matching well with ASTM reported data of pure PANI. The material was observed to be nanocrystalline in nature. There are no prominent peaks of CdO associated in XRD pattern of PANI due to smaller wt % of CdO in comparison with PANI. The grain size was determined by Scherrer's formula and found to be 40.26 nm.

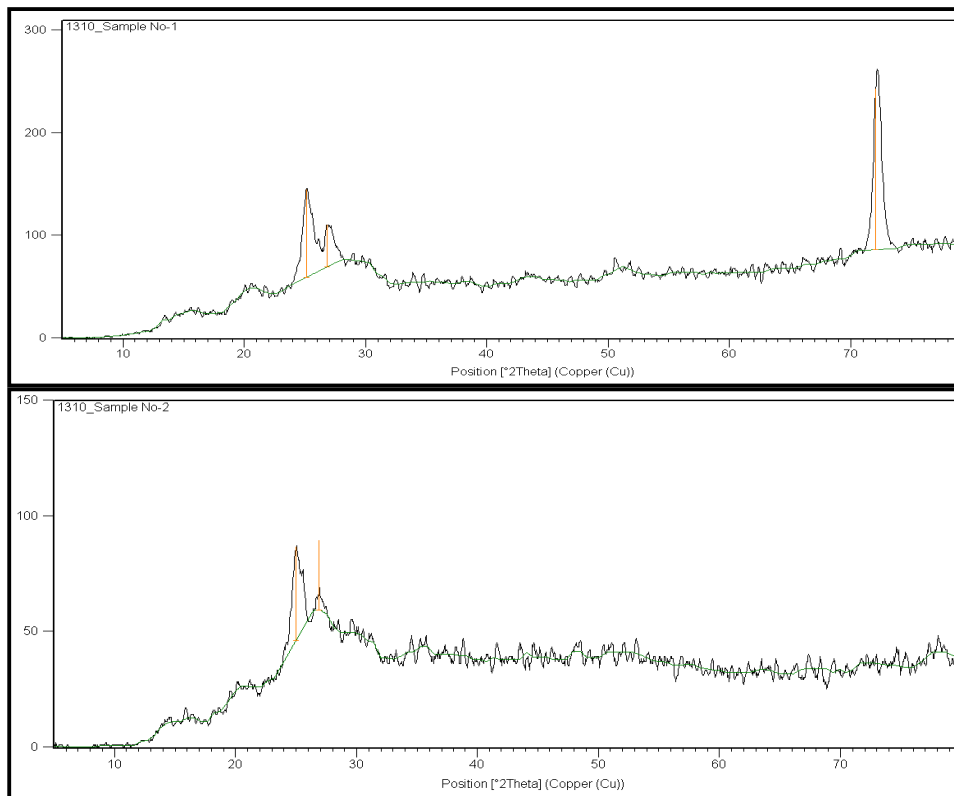


Fig. 1 XRD of pure and modified PANI/CdO

B. MICRO STRUCTURAL ANALYSIS (SEM)

Nova Nano FEG-SEM 450 with EDAX (Mapping System) facility was used to study sample size, shape, surface features at nano scale level along with elemental analysis.

The microstructure of pure and doped PANI thin film is shown in Figure 2 (a, b). In the micrograph of pure PANI, relatively bigger size particles were observed. While micrograph of the composite with 50 wt% CdO shows the interaction between particles in the PANI nano-composites with relatively smaller size particles which shows the presence of microcrystallites were are uniformly distributed and have higher porosity. A higher porosity usually led to a better response owing to a higher rate of gas absorption.

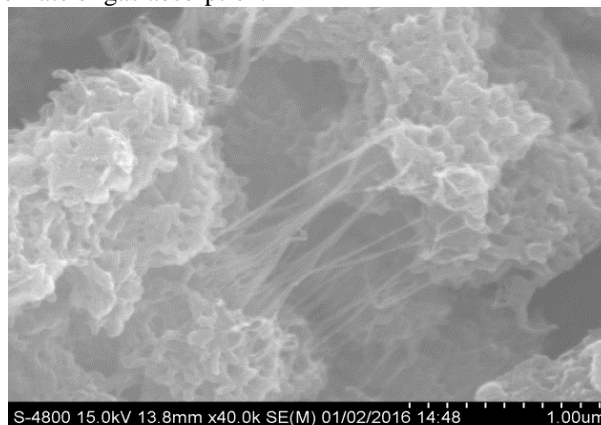


Figure: 2(a) SEM of pure PANI

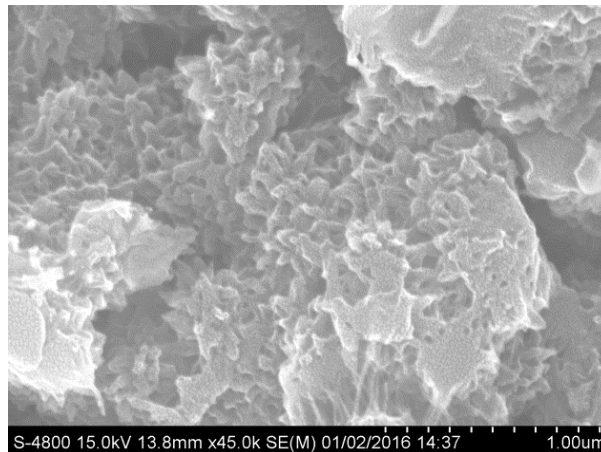


Figure: 2 (b) SEM of 50 wt% of CdO in PANI

C. TRANSMISSION ELECTRON MICROSCOPE (TEM):

Figure 3 shows the TEM images of the as-synthesized CdO nano particle. It is evident from these images that CdO nano material has rod-shaped nanostructures. Spherical particles have size distributions lie in the range of 16 - 23 nm. Spherical particles are assembled in a linear manner and make rod-shaped nano structure of 50 nm in length.

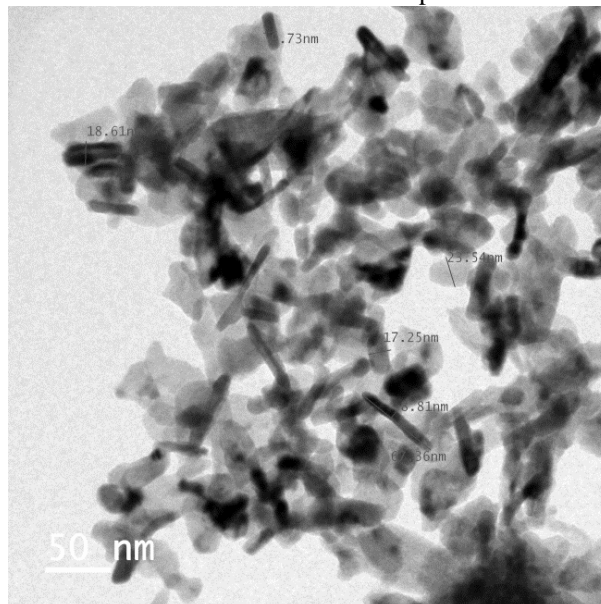


Figure: 3 TEM micrograph of CdO nanoparticles

D. FTIR ANALYSIS

The FTIR spectra of pure PANI nano-composite are shown in Figure 4 (a). The peaks at 520 cm^{-1} , 815 cm^{-1} are due to C-H out of plane bending vibration and para di-substituted aromatic rings, respectively. In-plane bending vibration in C-H occurs at 1163 cm^{-1} . The presence of bands in the range of $1450\text{-}1600\text{ cm}^{-1}$ were attributed to non-symmetric C_6 ring stretching modes.

Fig. 4 (b) shows the FTIR spectra of PANI/CdO 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 confirm the C-N stretching of primary aromatic amines. 1138.36 cm^{-1} reveals the C-H bending vibrations. The absorption bands lie below 1000 cm^{-1} is the characteristics of monosubstituted benzene [11]. For instance, C-N, C-N and C-C bonds are shifted to the higher wave numbers which are stronger in nano composites while N-H is shifted to the lower one which is weakened. According to the patterns, absorption intensity is increased by adding CdO nano rods in the case of nano composites due to uniform distribution of CdO nano rods in nano composites matrix and elimination of agglomeration.

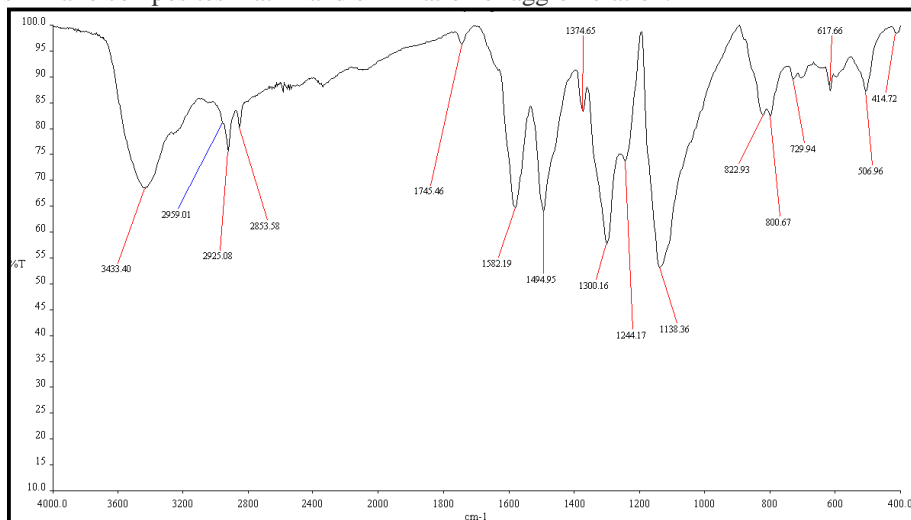


Figure: 4 (a) FTIR spectra pure PANI

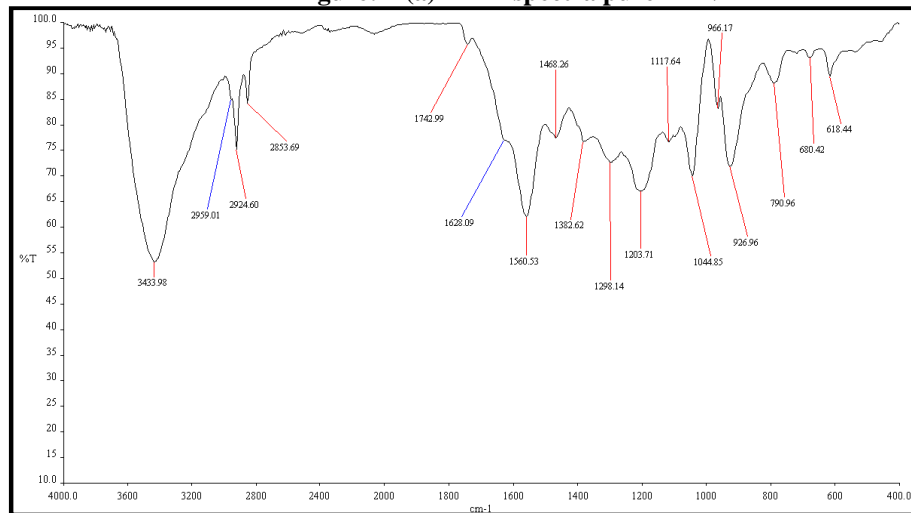


Fig: 4 (b) FTIR spectra of PANI/CdO nanocomposite (50 wt% CdO in PANI)

E. SENSOR RESPONSE TOWARDS HYDROGEN SULPHIDE:

Fig. 5 shows the exchange in electric resistance with awareness of H_2S in parts consistent with million at the steady quantity of natural PANI and PANI/CdO nanocomposites at room temperature (27°C). it is also located that amongst all the PANI/CdO nanocomposites, 40% and 50% nano composites shows a most change in resistance when as compared to natural PANI and different nano composites of different wt% of CdO in PANI (10, 20, 30 wt%).

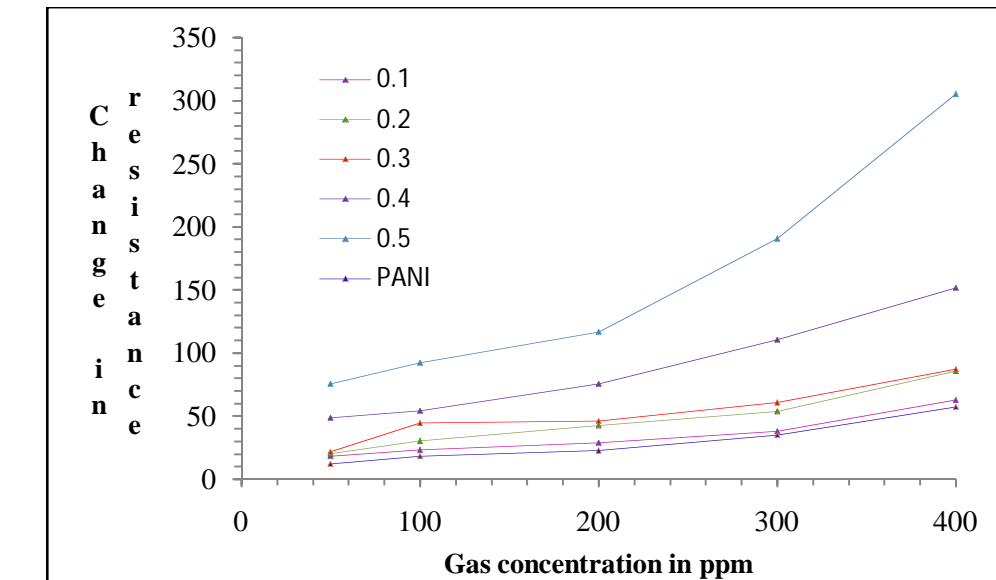


Figure 5: Sensitivity for various test gases at 400 ppm of H₂S gas

Fig. 6 shows the sensitivity in opposition to time for PANI/CdO nanocomposites. it's far found that the sensitivity lies between 150 to 305% at 400ppm for 40 and 50 wt % PANI/CdO nanocomposites while for PANI, 10, 20, 30 wt % nanocomposites sensitivity is less than 85%. The reaction time 16 sec at 400 ppm and healing time 6 sec at 400 ppm for PANI/CdO 50 wt% nanocomposite. The response within the resistance may be because of the adsorption of gas at the surface of the sensing materials which growth the scale of the sensing layer. The boom in extent reasons an increase in resistance which disturbs the conductive pathway through the fabric. While the gas is desorbed the polymer returns to its original length, restoring the conductive direction-methods. for this reason, electric resistance will increase with an increase in the awareness of gas.

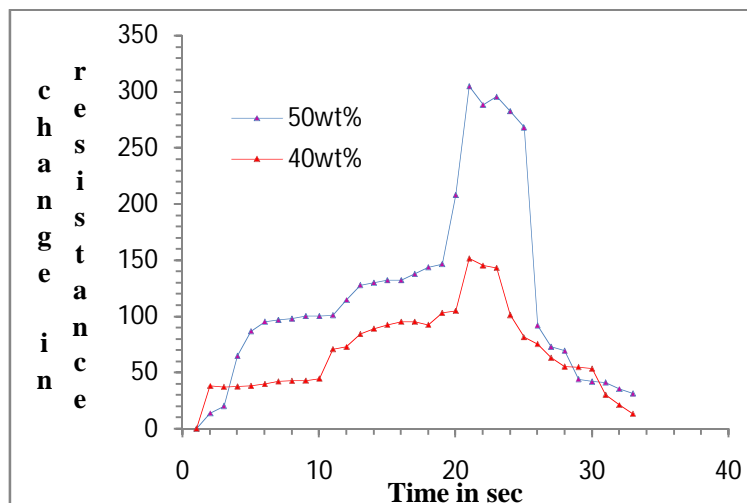


Figure 6: Recovery and response time of 40 and 50 wt% of CdO in PANI

Fig. 7 shows the version of selectivity of the PANI/CdO nanocomposites for diverse gasses inclusive of H₂S, CO₂, LPG and NH₃. it's miles discovered that the 50% PANI/CdO nanocomposites showed 60% reaction for CO₂ gas, 75%

for LPG, 90% for NH₃ while three hundred% for H₂S gasoline. The maximum response for H₂S gasoline may be because of interplay in CdO nanoparticles with H₂S and also due to oxidizing nature. For this reason, it's far one of the promising H₂S sensing substances for tool fabrication.

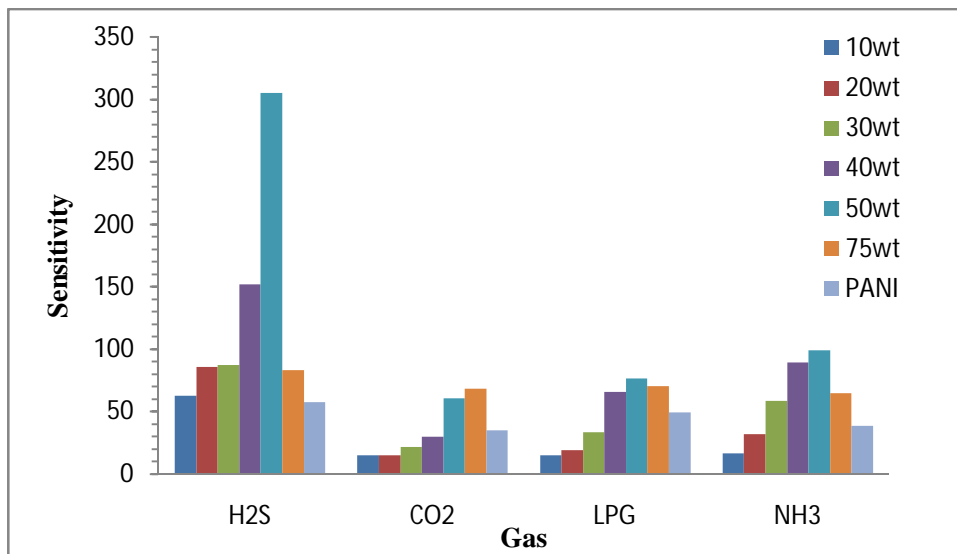


Figure 7: Variation of sensitivity for various gases test gases

F. SENSOR RESPONSE TOWARDS AMMONIA:

Figure 8(a) shows the change in electrical resistance with a concentration of NH₃ in parts per million at constant volume (ppm) of pure polyaniline and PANI/CdO composites at room temperature (27^oC). It is observed that when pellets were exposed to a gas, the polymer matrix swells. The increase in volume causes an increase in resistance due to this the conductive pathway through the material is disturbed. When the gas releases the polymer returns to its original size, restoring the conductive pathways. Thus electrical resistance increases with increase in the concentration of the gas. Also, among all the PANI/CdO composites, 40% and 50% composites show a maximum change in resistance as compared with pure PANI and other composites of 10, 20, 30 wt% of CdO in PANI. Fig. 8 (b) shows the sensitivity against time for PANI/CdO composites. For PANI, 10, 20, 30 wt % composites sensitivity is less than 83%. The response time is 30 second while the recovery time is 50 second at 400 ppm for PANI/CdO 50 wt% nanocomposite.

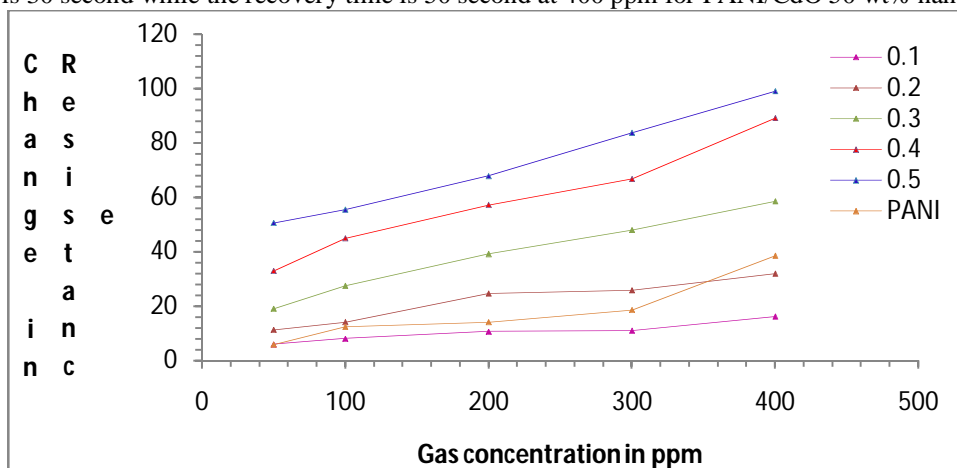


Figure 8 (a) Concentration ppm versus change in resistance

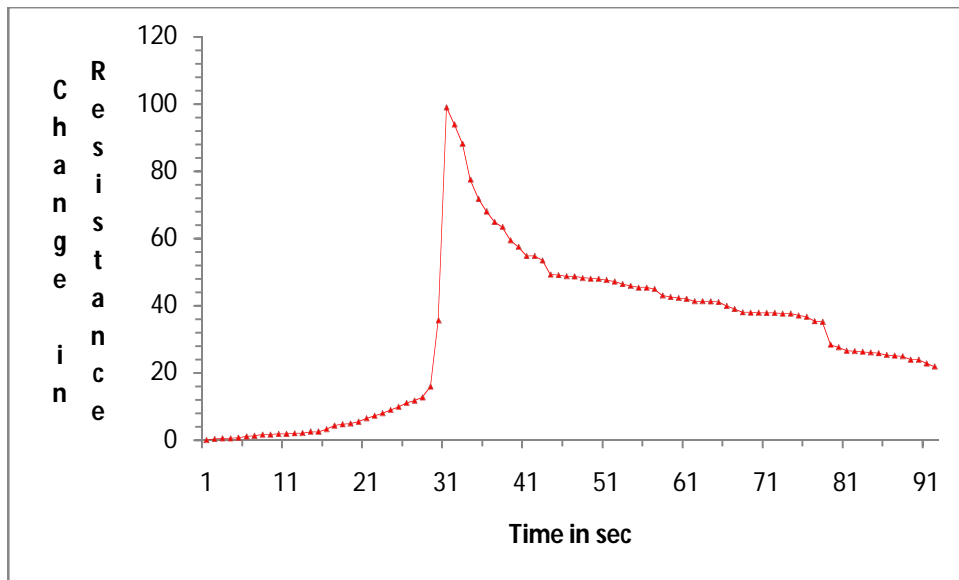


Figure 8(b) Response and Recovery time of 50 wt% of CdO in PANI

IV. CONCLUSION

CdO nanoparticles have been synthesized by a co-precipitate method using very easy, cheap and convenient process. XRD spectrum reveals that material is polycrystalline which is further confirmed by TEM analysis. SEM shows particles are uniformly distributed and highly porous in nature. TEM confirms the formation of rod shape of the nanocrystalline material. For H₂S the reaction time 16 sec at 400 ppm and healing time 6 sec at 400 ppm for PANI/CdO 50 wt% nano composite. The response within the resistance may be because of the adsorption of gas at the surface of the sensing materials which growth the scale of the sensing layer. For NH₃, the electrical resistance increases with increase in the concentration of the gas. Also, among all the PANI/CdO composites, 40% and 50% composites show a maximum change in resistance as compared with pure PANI and other composites of 10, 20, 30 wt% of CdO in PANI. The sensitivity against time for PANI/CdO composites. For PANI, 10, 20, 30 wt % composites sensitivity is less than 83%. The response time is 30 second while the recovery time is 50 second at 400 ppm for PANI/CdO 50 wt% nano composite.

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