ROOM TEMPERATURE AMMONIA GAS SENSING CHARACTERISTICS OF Co_3O_4

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Room temperature ammonia gas-sensing characteristics of Co_3O_4 pellet sensor are reported in this paper. For this purpose, Co_3O_4 powder is prepared by a route of simple precipitation + heating at $800°C/2$ hr. The as-prepared powder is characterized by using X-ray diffraction and scanning electron microscopy. The ammonia gas-sensing properties of Co_3O_4 pellets made at various loads of 3, 5, 7 & 9 ton and at constant time = 4 min. are measured using home-built static gas sensing system. The characterization studies revealed that the cobalt oxide particles formed are cubic spinel Co_3O_4, highly pure and spherical in shape. The particle size distribution is found to be nearly uniform with average particle size ~ 1 µm. The ammonia gas sensing properties of Co_3O_4 pellet sensor are found to be good. The highest sensitivities − S.F. = 175 and 358 are found at ~ 25 ppm and 250 ppm concentrations of ammonia gas respectively for the Co_3O_4 pellet sensor made at the load = 3 ton. Further, an admirable repeatability and reversibility in the ammonia gas sensing characteristics are observed for all the Co_3O_4 pellet sensors. The average response time of 4.0 min. and recovery time of 3.0 min. are obtained for all the Co_3O_4 pellet sensors.

Keywords: *Co_3O_4, AMMONIA SENSOR, SENSITIVITY, REPEATBILITY, RESPONSE & RECOVERY TIME.*

1. INTRODUCTION

The ecosystem is adversely affected owing to discharge of untreated effluent waste as well as toxic gaseous exhaust from the automobile and chemical industry. In order to detect, measure and control the release of toxic gases into the environment, one should know the amount and type of gases present in the atmosphere. Therefore, the need to monitor and control these gases has led to the research and development of very large variety of

sensors using different materials and technologies. Sensors are basically used for measurement of physical quantities and for controlling systems. Sensors play an important role in the areas of emissions control, environmental protection, public safety and human health [1-4].

Presently, the development of sensors with both high sensitivity and rapid response is a serious environmental issue. In addition to in-depth exploration of gas-sensing mechanisms [5] and innovative sensor device design [6], a variety of novel gas sensors based on metal oxides such as SnO_2 [7], In_2O_3 [8], Fe_2O_3 [9], WO_3 and ZnO [10] etc., have been successfully fabricated & vigorously tested and have also proven to be excellent. Recently, the materials with ultra-high surface to volume ratio(s) are found to be excellent candidates for gas-sensing applications in view of their surface driven change in electrical properties arising due to surface-adsorbed species [11, 12]. For developing a low temperature gas sensor, it is imperative to consider issues such as (i) reproducibility of output on consecutive measurements and (ii) good sensitivity of material and rate of chemisorptions & surface reactions at low temperature. However, most of the efforts in the field of sensors are related to the development of gas sensors based on n-type semiconductor metal oxides, while the sensing properties of the p-type semiconductor metal oxides are scarcely investigated.

Co_3O_4 is an anti-ferromagnetic semiconductor having energy band gap ranging from 1.4 to 1.8 eV. It is normally non-stoichiometric in nature with an excess of oxygen, and displays p-type semiconductor behavior. Co_3O_4 are extensively used in glass industry for imparting colour and as a catalytic activator in chemical processes for oxidation reactions [13]. Co_3O_4 is a strong catalyst for ammonia oxidation reactions. Hence, Co_3O_4 might turn out to be a promising material for the fabrication of low temperature ammonia sensors [14, 15]. Further, the reports on ammonia gas sensing characteristics of Co_3O_4 particles are not available in literature. In view of this, the main objective of present work was to study the gas-sensing properties of Co_3O_4 particles for ammonia.

2. EXPERIMENTAL

2.1 Material preparation

Cobalt oxide (Co_3O_4) powder was prepared by simple precipitation method. Solution of cobalt sulphate ($CoSO_4$) was prepared in double distilled water. To this solution, sodium hydroxide (NaOH) solution in double distilled water was added drop by drop. The pH of solution was maintained at 12 [16, 17]. The precipitate obtained was washed with double distilled water and dried at 75 °C to get dry powder. The dry powder was ground to obtain fine powder. This dry powder was heated at 800 °C for 2 hr to obtain cobalt oxide powder. The heated powder was used to make the pellets (each of wt. = 0.5 gm and diameter = 10 mm) for ammonia gas sensing studies. The pellets were made by using hydraulic press at different times = 0.5, 1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 min. but at constant load = 7 ton. The pellets were also made at different loads = 3, 4, 5, 6, 7, 8 and 9 ton but at constant time = 4 min. Electrical contacts were given to the either side of each pellet using silver paste. To obtain good ohmic contacts the pellets were cured at 600 °C for 30 min.

2.2 Material characterization

The heated powders were characterized by using different physical techniques. The X-ray diffractometer (Bruker AXS, D8 Advance) was used for phase analysis of powders using CuK_α radiation ($\lambda = 1.5405$ Å). The scanning electron microscopy (JEOL, JEM 6360) was used for the morphological studies (particle size, shape, size distribution etc.) of heated powders.

2.3 Gas sensing properties

Ammonia gas sensing properties of different pellets were measured by using home-built static gas sensing system at room temperature (RT). Figure 1 gives the schematic diagram of home-built static gas sensing system.
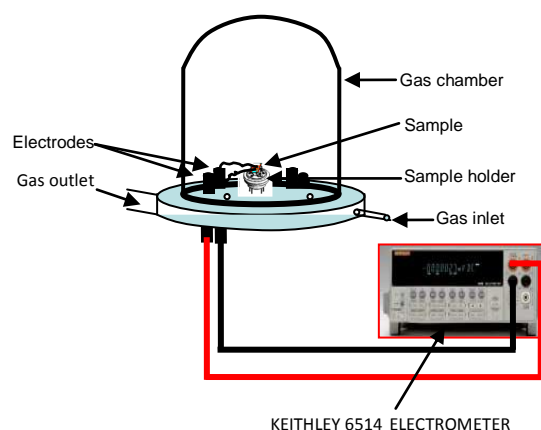

Fig. 1 − Schematic diagram of home-built static gas sensing system

The pellet was mounted on the sample holder. The desired amount of gas concentration (ppm) inside the chamber was achieved by injecting a known volume of an ammonia gas with the help of gas injecting syringe through a inlet valve of the chamber fitted at one of the ports of the base plate. The change in electrical resistance of the pellet in the presence of ammonia gas was measured with the help of multi-meter (Keithley, Model 6514, System Electrometer). The gas sensing properties of different pellets (obtained at different loads of 3, 5, 7 and 9 ton) were measured at different concentrations of ammonia gas ranging from ∼ 25 ppm to 250 ppm. The gas sensing response i.e. sensitivity factor (S.F.) was obtained by using the formula − S.F. $= [(R_a − R_g)\cdot 100]/R_a$, where, $R_a =$ resistance of pellet in air and $R_g =$ resistance of pellet in gas.

To check repeatability & reproducibility, to obtain response time (RST) (time needed for a sensor to attain the maximum change in resistance) and to obtain recovery time (RCT) (time needed for a sensor to get back 80 % of the original resistance) [18, 19], the gas sensing curves were recorded at 250 ppm for 12 cycles for the pellets obtained at the loads of 3, 5, 7 and 9 ton.

3. RESULT AND DISCUSSION

3.1 X-ray diffraction studies

Figure 2 shows the X-ray diffraction pattern of powder heated at 800 °C. The diffraction peaks corresponding to the Cobaltous oxide: CoO [JCPDS, PDF-71-1178] with face centered cubic symmetry and cobalt oxyhydroxide: CoO(OH) [JCPDS, PDF-74-1057] with hexagonal symmetry are not observed in the diffraction pattern given in Figure 2. All the reflection lines match with the diffraction peaks given in JCPDS data file for Co_3O_4 [PDF-76-1802/ JCPDS Card No 43-1003] with cubic spinel symmetry [20, 21]. The lattice parameter calculated from the (400) reflection plane was found to be 8.068 Å, which is very close to the reported value of 8.084 Å for Co_3O_4 phase with cubic spinel symmetry [22, 23]. This clearly indicates the formation of single phase Co_3O_4 in the powders prepared in present work.
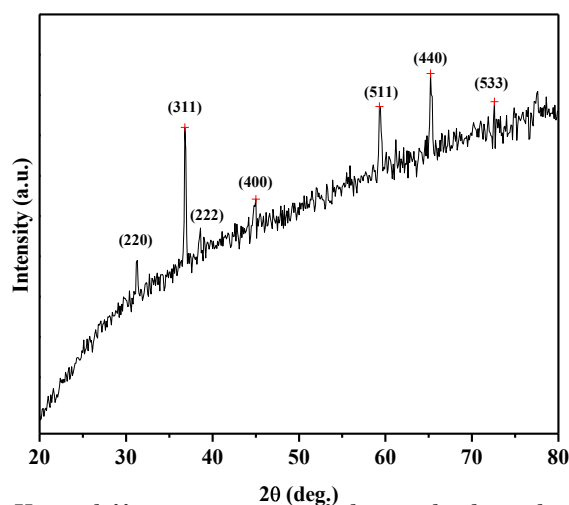

Fig. 2 − *X-ray diffraction pattern of the powder heated at* 800 °C

3.2 Scanning electron microscopy studies

Figure 3 (a) and (b) give the scanning electron microphotographs of Co_3O_4 powders obtain in the present work at two different magnifications. Following observations are noted from the microphotographs: (1) shapes of the particles are nearly spherical, (2) particle size distribution is also nearly uniform, (3) interfusion of particles is giving the rod shape to the some particles, (4) all the particles are dense micro-grains, (5) no hard agglomerates are present in the any part of powder and lastly (6) the average particle size is found to be ~ 1 µm.

3.3 Optimization of pelletization conditions

Figure 4 gives the variation of resistance of pellet (in MΩ) versus the time used for pelletizing at the constant applied load = 7 ton. From figure it is clear that resistance (in MΩ) of pellet decreases exponentially with increasing the pelletizing time from 0.5 min. to 5 min. This decrease in resistance can be attributed due to increase in green density of pellet and increase in grain-grain

contacts or decrease in grain boundaries. The resistance of pellet remains constant and at minimum value = 6137 MΩ for the pelletizing time = 4 min and above. Hence, pelletizing time = 4 min. is used for making the pellets at different load from 3 to 9 ton.
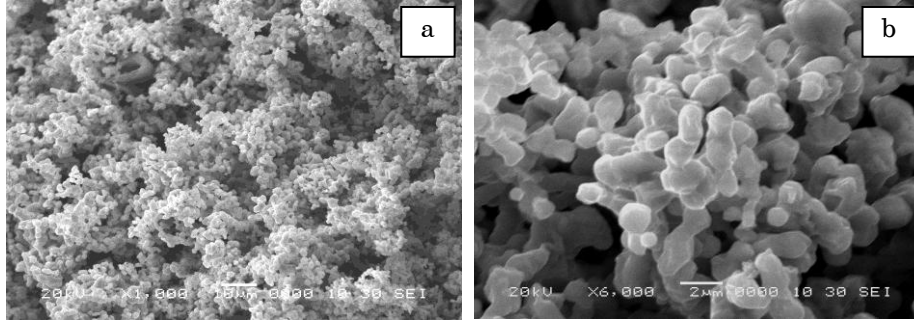

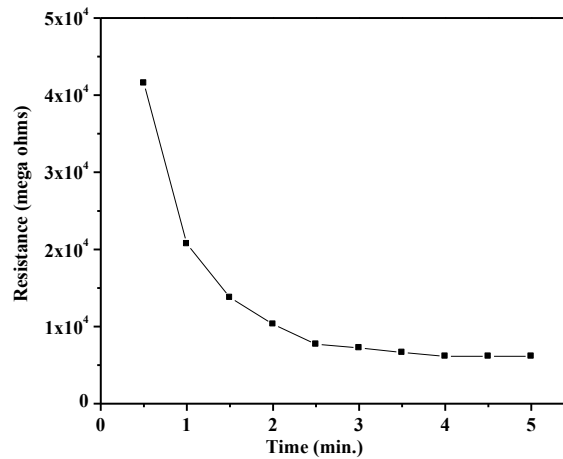*Fig. 3 − Scanning electron microphotographs of Co_3O_4 powder under two different magnifications*

Fig. 4 − Variation of resistance of pellet (in MΩ) vs. the pelletizing time at the constant applied load = 7 ton

Figure 5 gives the variation of resistance of (in MΩ) versus the load applied for making the pellets at the constant pelletizing time = 4 min. Similar observations as mentioned-above are also noted in this case. Resistance of pellet found to be decreasing exponentially with the load applied for pelletization. This might be due to more densification and thereby decrease in grain boundaries percentage in the resultant pellets. Resistance of the pellet was found to be almost constant and at minimum value = 6137 MΩ for the pellets made at the load = 6.5 ton and above. This optimization is just to obtain the pellets with having good mechanical strength
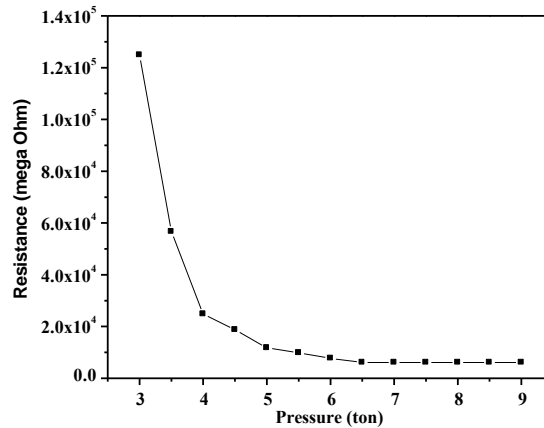
Fig. 5 − Variation of resistance of (in MΩ) vs. the load applied for making the pellets at the constant pelletizing time = 4 min.

3.4 Gas sensing properties

Figure 6 gives the variation of sensitivity factor (S.F.) versus ammonia gas concentration in gas sensing chamber at room temperature (RT) for the different pellets obtained at various loads of 3, 5, 7 and 9 ton.
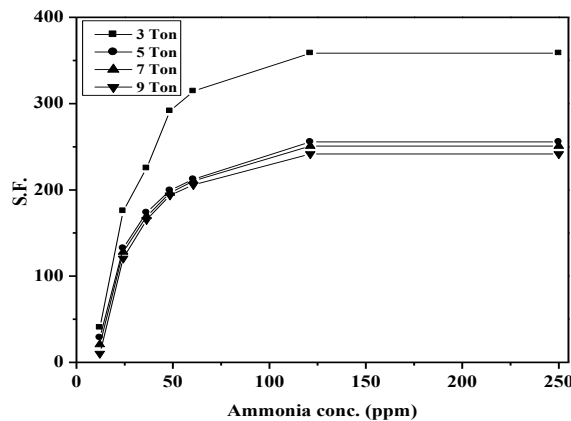

Fig. 6 − Variation of sensitivity factor (S. F.) vs. ammonia gas concentration in gas sensing chamber at RT for the different pellets of Co_3O_4 obtained at various loads of 3, 5, 7 and 9 ton

Similar trends are observed in the variation of S.F. with ammonia gas concentration for all the pellets. The S.F. is increasing exponentially upto 60 ppm of ammonia gas and then it saturates to different fixed values for different pellet sensors. Above 120 ppm of ammonia gas, the S.F. remains constant. Further, the variation of S.F. with gas concentration is almost same for the pellets obtained at the loads of 5, 7 and 9 ton. The maximum values of S.F. = 255.70, 250.80 and 241.57 are obtained at 121 ppm of ammonia gas concentration for the pellets made at loads of 5, 7 and 9 ton respectively. This decrease in S.F. with increase in load is expected because with increase in load

the green density of pellet increases and porosity & hence the surface area per unit volume reduces. The maximum S.F. = 358.50 is obtained at 121 ppm for the pellet generated at load = 3 ton. Furthermore, the sensitivities of all pellets are also very good at very low ammonia gas concentration ~ 25 ppm. The high S.F. = 175.75, 132.35, 127.91 and 120.50 at room temperature (RT) are found for the pellets made at loads of 3, 5, 7 and 9 ton. This proves the ammonia gas sensing potential of Co_3O_4 pellet sensor prepared in the present work. For each pellet sensor, the S.F. increases with increasing the ammonia gas concentration. This is due to the increase in room temperature conductivity of each pellet with increases gas concentration.

In order to check the repeatability in the gas sensing response and to find the response & recovery times of different sensor pellets, the ammonia gas sensing responses are recorded for 12 cycles at RT and at gas concentration = 250 ppm for the pellets obtained the loads of 3, 5, 7 and 9 ton. The ammonia gas concentration = 250 ppm was chosen because the stable and maximum values of S.F. are recorded (Figure 6) at this concentration of gas. Figure 7 (a), (b) (c) and (d) give the variation of resistance versus time for 12 cycles for the pellets obtain at load = 3, 5, 7 and 9 ton respectively.
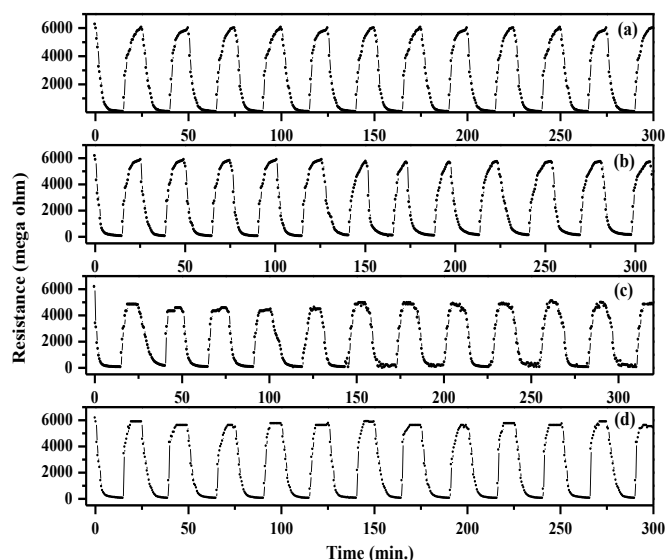

Fig. 7 − *Variation of resistance vs. time for* 12 *cycles for the* Co_3O_4 *sensor pellets obtain at different loads of (a)* 3, *(b)* 5, *(c)* 7 *and (d)* 9 *ton*

From Figure 7 (a), (b), (c) and (d) following important observations are noted. A high repeatability in the gas sensing response is observed for all the sensor pellets, and at the end of each cycle the original conditions are recovered. Further, the trend in variation of resistance with respect to time is almost repeated in the successive cycles for each sensor pellet. This may indicate the good life time for each sensor pellet. It was observed that the response and recovery times of a given sensor pellet are almost same for all cycles. Further, the response and recovery times for all the sensor pellets are also almost same. An average response time of 4.0 min. and recovery

time of 3.0 min. are obtained for all the sensor pellets. These high values of response and recovery times are also matching with the reported data [24].

The repeatability in gas sensing response of given sensor pellet at different gas concentration is also checked. The figure 8 gives the variation in resistance with respect to time for four different cycles of gas sensing response for a sensor pellet obtained at load = 7 ton. The four cycles of gas sensing are recorded at four different concentrations − 24.24 ppm, 60.60 ppm, 120 ppm and 250 ppm of ammonia gas. Figure 8 and figure 6 clearly indicate the repeatability in a gas sensing response of a given sensor pellet of 7 ton. With decreasing the ammonia gas concentration, the change in resistance thereby conductivity and hence the S.F. is also decreasing. This is observed in Figure 8.
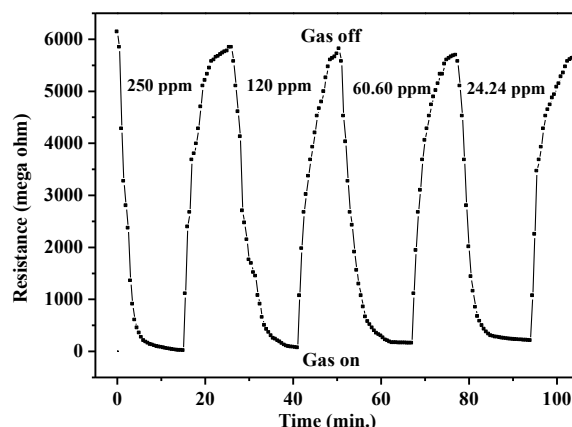

Fig. 8 − Variation of resistance vs. time for four different cycles at four different ammonia gas concentration for a Co_3O_4 *sensor pellet made at load = 7 ton*

4. CONCLUSIONS

Room temperature ammonia gas-sensing characteristics of Co_3O_4 pellet sensor are found to be good. The highest sensitivities − S.F. = 175 and 358 are found at ~ 25 ppm and 250 ppm concentrations of ammonia gas respectively for the Co_3O_4 pellet sensor made at the load = 3 ton. Further, an admirable repeatability and reversibility in the ammonia gas sensing characteristics are also noted for all the Co_3O_4 pellet sensors. The average response time of 4.0 min. and recovery time of 3.0 min. are obtained for all the Co_3O_4 pellet sensors.

Hence, the Co_3O_4 pellets made in the present work could be used as an admirable ammonia gas sensing material at room temperature.

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