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Effect of temperature on the gas sensing properties of the cobalt ferrite nanoparticles

Shinde S. A. and Raut S. D.

Department of Physics, Sharadchandra Arts, Commerce and Science College, Naigaon, Dist. Nanded-431709.

Abstract

The effect of the temperature on the gas sensing properties of the cobalt ferrite nanoparticles ($CoFe_2O_4$ NPs) has been studied and reported. The $CoFe_2O_4$ NPs were prepared using sol-gel auto-combustion synthesis technique. The confirmation of the structural and morphological properties of the prepared $CoFe_2O_4$ NPs were carried out using various characterization technique like X-Ray diffraction analysis (XRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET). The prepared $CoFe_2O_4$ NPs were further utilized to study the gas sensing properties against various volatile compounds (VOCs) *viz*. ethanol, methanol, acetone, ammonia, and toluene. The $CoFe_2O_4$ NPs were found responsive to ammonia as compared to the rest of the VOCs. Afterwards, the $CoFe_2O_4$ NPs were tested at various temperature i. e. room temperature (RT- 25), 50, 100, 150, and 200°C. against ammonia. It was found that the $CoFe_2O_4$ NPs shows 76.36% response against ammonia at 100 °C. All the measurements were carried out at 100 ppm concentration of all the VOCs. Moreover, the $CoFe_2O_4$ NPs shows excellent stability of 85.76% even after 15 days. The present study will be a good lead for the further research in the field.

Introduction

Gas sensors are crucial for a variety of reasons, including safety, environmental monitoring, process control, medical diagnostics, and agriculture. They provide real-time feedback on gas levels, allowing for proactive measures to be taken to prevent negative outcomes [1, 2]. In industries such as oil and gas, mining, and chemical manufacturing, gas sensors are essential for detecting the presence of hazardous gases that could be harmful or even deadly to workers [3, 4]. In environmental monitoring, gas sensors are used to assess air quality and make informed decisions about pollution control measures. In manufacturing processes, gas sensors ensure the precise control of gas levels to maintain optimal conditions [5]. In medical diagnostics, gas sensors measure the levels of various gases in a patient's breath, helping to diagnose conditions such as asthma and sleep apnea. In agriculture, gas sensors are used to monitor gas levels in livestock environments and optimize plant growth in greenhouses [6]. Overall, gas sensors are necessary for ensuring safety, protecting the environment, optimizing manufacturing processes, and improving health outcomes. In industrial settings, ammonia gas sensors are critical for worker safety. Ammonia gas is commonly used in refrigeration systems, and leaks can be extremely dangerous, leading to respiratory issues, burns, and even death. Ammonia sensors provide real-time feedback on gas levels, allowing for immediate action to be taken to prevent negative outcomes. In agricultural settings, ammonia gas sensors are used to monitor gas levels in livestock environments [7]. High levels of ammonia can cause respiratory issues in animals, leading to decreased productivity and increased health risks. By monitoring ammonia gas levels, farmers can take proactive measures to ensure animal health and safety [8]. Overall, ammonia gas sensors play a critical role in ensuring safety and improving environmental conditions. They provide real-time feedback on ammonia gas levels, allowing for proactive measures to be taken to prevent negative outcomes in industrial and agricultural settings.

The cubic spinel ferrites have garnered significant interest for their potential applications in microelectronics, magnetism, catalysis, and gas sensing. These materials possess desirable electronic, magnetic, and catalytic properties [9–12]. Several synthetic strategies have been reported in the literature for the synthesis of $CoFe_2O_4$ nanoparticles, including oil-in-water micelle [13], hydrothermal [14], co-precipitation [15], and sol-gel auto-combustion [16]. Among these methods, sol-gel auto-combustion offers several advantages, such as the use of inexpensive precursors, ease of operation, low calcination temperature, high energy efficiency, and the production of nanoparticles with a fine size distribution and exceptional chemical homogeneity [17]. Upon exposure to a gas flow, the conductivity/sensitivity of cubic spinel ferrite nanoparticles changes due to the interaction of their atoms with gas molecules.

Raut et al. investigated the ammonia sensing performance of $CoFe_2O_4$ nanoparticles synthesized *via* sol-gel method. They also studied the effect of gamma radiation on the sensing performance of these nanoparticles. The bare $CoFe_2O_4$ nanoparticles exhibited a response of 24% towards 100 ppm ammonia with a response time of 95 seconds and a recovery time of 250 seconds. The ammonia sensing performance of the nanoparticles was enhanced with gamma radiation treatment [18]. In a separate study, Prasad et al. prepared $CoFe_2O_4$ nanoparticles via electrospinning and evaluated their response towards ammonia at room temperature. The nanoparticles showed a response of 0.42 towards 900 ppm ammonia. Based on these results, it is clear that there is scope for improving the gas sensing performance of $CoFe_2O_4$ nanoparticles [19].

In the present study, we report on the improvement of the gas sensing performance of $CoFe_2O_4$ nanoparticles via heat treatment. The ammonia sensing performance of the nanoparticles was measured at various temperatures. The pristine nanoparticles exhibited an excellent response of 76.36% at 100 ppm ammonia concentration at 100°C which is much better than the room temperature response. These results suggest that the gas sensing performance of various nanostructures could be improved using similar approaches.

Experimental details

The synthesis of $CoFe_2O_4$ nanoparticles was carried out using a sol-gel auto-combustion method. Stoichiometric amounts of cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$], ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$], and citric acid monohydrate [$C_6H_8O_7 \cdot H_2O$] were mixed together while continuously stirring. The pH of the solution was adjusted to 7.0 using liquor ammonia. Citric acid acted as a fuel to prevent the metal ions from precipitating as metal hydroxides, thus promoting the necessary bonding between the metal ions [20]. The resulting precursors were magnetically stirred for 2 hours at a temperature of 80-90°C to obtain a homogeneous gel with a high viscosity. The gel was then burned until it turned into ash, which was subsequently annealed at 500°C and ground into a powder form to obtain cobalt ferrite.

Characterizations

The structural and morphological properties of the synthesized $CoFe_2O_4$ nanoparticles were characterized using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET) measurements. The gas sensing measurements were performed using a Keithley source meter.

Formulae used

The sensor response was calculated by using following formula [18]:

$$\text{Response (\%)} = \frac{R_a - R_g}{R_a} \tag{1}$$

Were,

R_a- resistance in air, and

R_g- resistance in presence of target gas.

The concentration of the target gas has been calculated using the formula [18],

$$C\ (ppm) = \frac{22.4\ \rho T V\prime}{273\ MV} \times 100 \tag{2}$$

Where,

C- concentration of target gas (ppm),

P- density of the liquid ammonia (g/ml),

V'- volume of the liquid ammonia (μl),

T- temperature (K),

M- molecular weight of the liquid ammonia (g/mol), and

V- volume of the testing chember (L).

Results and discussion

Structural and morphological study

The X-ray diffraction (XRD) patterns of the prepared $CoFe_2O_4$ nanoparticles are presented in Fig. 1a. All XRD peaks corresponding to (111), (220), (311), (400), (422), (511), (440), (533), and (731) planes are in good agreement with the JCPDS-22-1086, confirming the formation of phase-pure $CoFe_2O_4$ nanoparticles.

The surface morphology of the $CoFe_2O_4$ nanoparticles is shown in Fig. 1b. Scanning electron microscopy (SEM) images revealed agglomerated and randomly distributed nanoparticles. The observed agglomeration in the SEM images may be attributed to the humid climate, which is unavoidable.

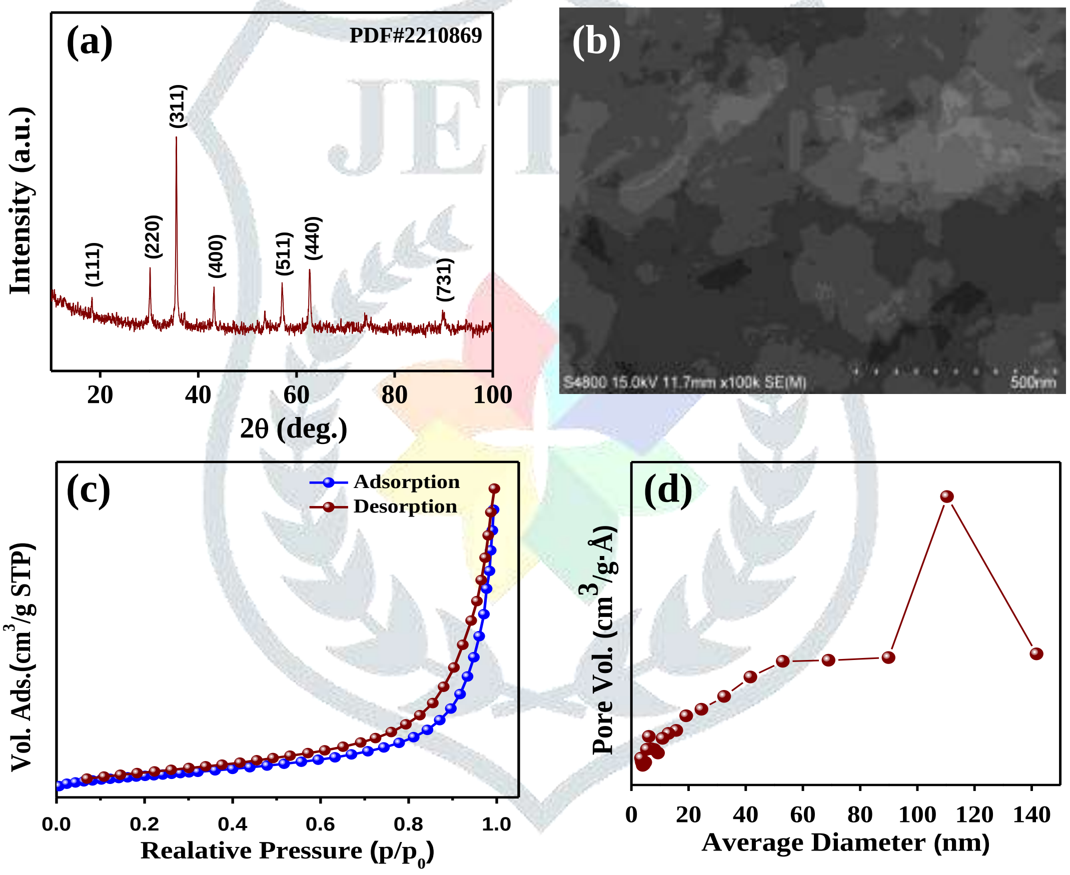

Figure 1: The XRD pattern, (b) SEM image, (c) BET graphs, and (d) pore-size distribution of the $CoFe_2O_4$ nanoparticles.

The surface area of the $CoFe_2O_4$ nanoparticles was calculated using BET (Brunauer-Emmett-Teller) measurements and is depicted in Fig. 1c. The surface area of the prepared $CoFe_2O_4$ nanoparticles was found to be 22.15 m^2/g. The BJH (Barrett-Joyner-Halenda) pore size distribution is shown in Fig. 1d, revealing an average pore diameter of 110.55 nm, indicating the microporous nature of the pristine $CoFe_2O_4$ nanoparticles.

Gas sensor properties

The gas sensor performance of the prepared $CoFe_2O_4$ nanoparticles was measured using a Keithley source meter. The resistance of the $CoFe_2O_4$ nanoparticles was observed to vary, which is attributed to the adsorption and desorption of molecules from the target gas. The initial study of the gas sensor performance involved testing the $CoFe_2O_4$ nanoparticles with volatile compounds (VCs) such as ammonia, acetone, toluene, methanol, and ethanol. The results of this study are shown in Fig. 2.

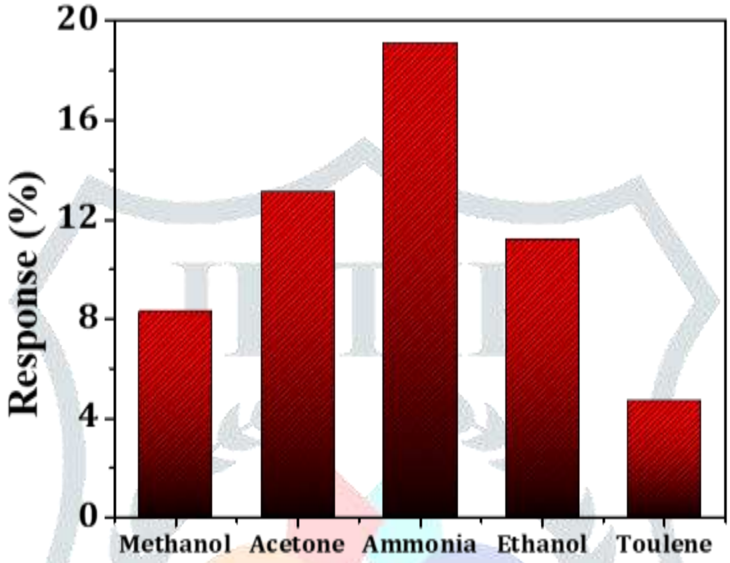

Figure 2: The selectivity of the $CoFe_2O_4$ nanoparticles against various target VCs at room temperature.

Among the tested VCs, $CoFe_2O_4$ nanoparticles shows highest response of 19.08%. Based on the selectivity, further measurements were carried out for ammonia only.

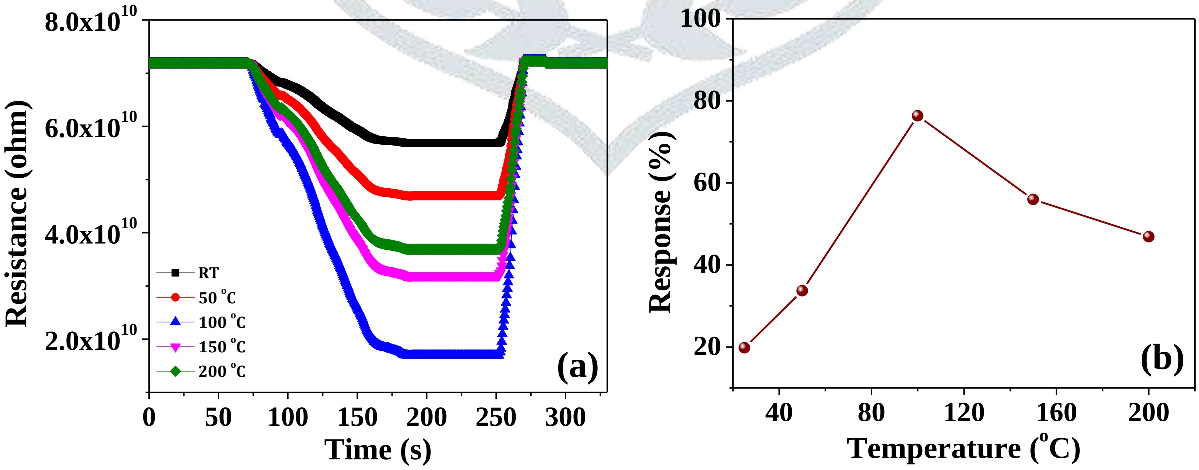

Figure 3: The effect of temperature on the gas sensing performance of the $CoFe_2O_4$ nanoparticles against ammonia.

The effect of temperature on the gas sensing performance of $CoFe_2O_4$ nanoparticles against ammonia is depicted in Fig. 3. Fig. 3a illustrates the resistance variation as a function of temperature, while Fig. 3b shows the response variation of the $CoFe_2O_4$ nanoparticles against ammonia at different temperatures: room temperature (RT), 50°C, 100°C, 150°C, and 200°C.

The results indicate that the prepared $CoFe_2O_4$ nanoparticles exhibit the highest response of 76.36% at 100°C, which can be attributed to the presence of active sites on the material surface. However, the response of the $CoFe_2O_4$ nanoparticles decreases significantly at other temperatures: RT (19.80%), 50°C (33.7%), 150°C (55.95%), and 200°C (46.85%). Consequently, measurements were carried out up to 200°C, as the response of the nanoparticles continued to decrease beyond this point.

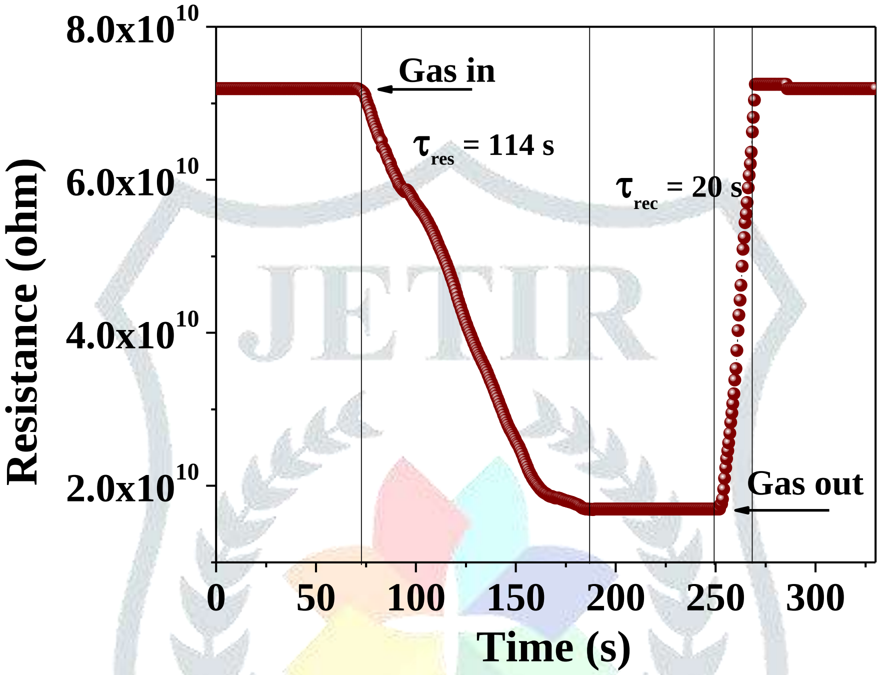

Figure 4: The response/recovery of the $CoFe_2O_4$ nanoparticles against ammonia at 100°C.

Additionally, the response and recovery of the $CoFe_2O_4$ nanoparticles against ammonia were measured and reported (Fig. 4). The highest response of 76.36% was recorded at 100°C. The response time of the ammonia sensor was found to be 114 seconds, while the recovery time was observed to be 20 seconds, which is significantly faster than the response time. The rapid recovery of the $CoFe_2O_4$ nanoparticles' ammonia sensor can be attributed to the fast adsorption of ammonia molecules from the material surface.

The durability of the $CoFe_2O_4$ nanoparticles against ammonia at 100°C was found to be 85.76% after 15 days and shown in Fig. 5. The ammonia sensor based on $CoFe_2O_4$ nanoparticles remained considerably stable even after 15 days of continuous operation, indicating the suitability of the temperature range for effective adsorption and desorption of ammonia molecules.

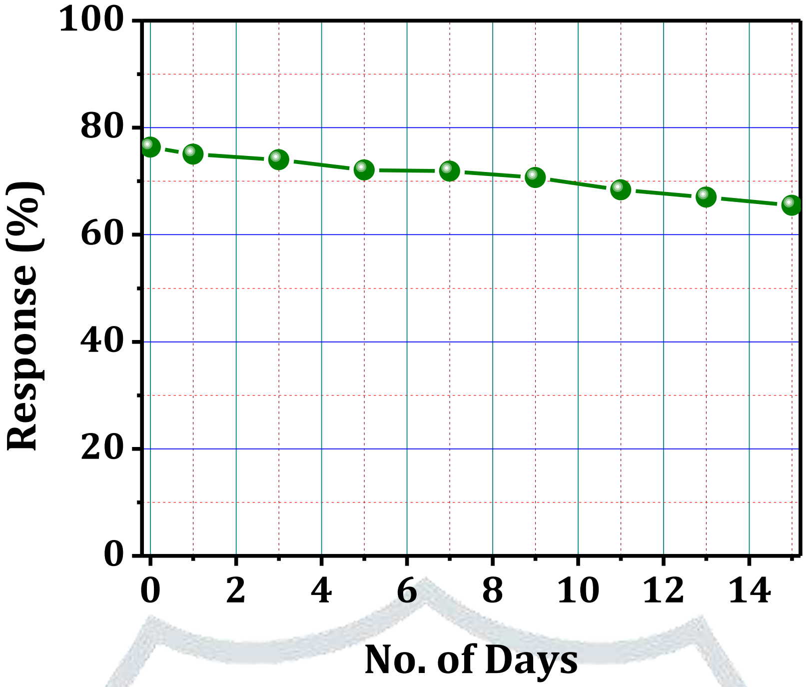

Figure 5: The durability test of the $CoFe_2O_4$ nanoparticles ammonia sensor.

Conclusions

The current study investigates the gas sensing performance of sol-gel mediated randomly distributed $CoFe_2O_4$ nanoparticles specifically for ammonia detection, with a focus on the influence of temperature. Additionally, the sensor performance of the $CoFe_2O_4$ nanoparticles was evaluated for various volatile organic compounds (VOCs) at different temperatures. Notably, the $CoFe_2O_4$ nanoparticles exhibited a significant response to ammonia compared to the other tested VOCs. The ammonia sensor based on $CoFe_2O_4$ nanoparticles demonstrated exceptional enhancement, displaying a remarkable 76.26% response at 100°C. This high response can be attributed to the efficient adsorption and desorption of ammonia molecules, which also contributed to the sensor's response and recovery time. The $CoFe_2O_4$ nanoparticles ammonia sensor exhibited a noteworthy response time of 114 seconds and a recovery time of 20 seconds. These findings provide valuable insights for further improving sensor response using similar approaches, making the present study a significant step in that direction.

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