Development of metal oxide based formaldehyde (HCHO) sensors using laser ablated nanoparticles

A Thesis submitted by

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Conclusions and Future Work

7.1 Conclusions

In this thesis work, the recent progress and remarkable development in the gas sensing field (especially for formaldehyde sensing) by using laser ablated nanoparticles were presented. Metal oxide nanoparticles (ZnO, NiO etc.) were synthesized in air using the laser ablation method for the rapid prototyping of formaldehyde sensors and a new surface decoration technique was optimized for the fabrication of heterojunction (ZnO/SnO_2, NiO/SnO_2) based sensor. The observed results confirm the potential of formaldehyde sensing application using metal oxide nanoparticles. To address the current requirement of fast, and cost-effective synthesis method for metal oxide nanoparticles for gas sensing applications, this thesis work provides a valuable outcome in terms of gas sensing performance optimization. All outcomes of this thesis work are summarized given below:

Some key issues and problems for the development of formaldehyde sensors using metal oxide material are addressed in the Chapter 1.

The material synthesis, characterization and device fabrication tasks involve a large number of equipment and characterization systems. The use of these instruments requires a basic understanding of working principles. Thus, in chapter 2, we explained all the techniques used during the various stages to carry out the presented work. It includes wafer cleaning procedure, annealing of devices using furnace and oven, RF-sputtering, XRD, FESEM, AFM, electrical (I-V) measurement facility, gas sensor characterization set-up etc.

Challenges to develop an efficient microheater by ablation of Au metal thin film using a Q-switched nano-second laser for gas sensing platform are discussed in chapter 3. Further in this chapter, we discussed all the exciting results (long-term reliability in self-heating mode) using an indigenous gold microheater which showed the potential of a metal oxide based gas sensor platform. We also discussed the potential of commercially available Ni-Cr heater based gas sensor platform for the rapid growth of formaldehyde gas sensor platforms.

Next, SnO_2 thin film metal oxide based sensor was fabricated on Ni-Cr based commercial gas sensor platform and the formaldehyde sensing properties of SnO_2 thin film sensor was explored in Chapter 4. The SnO_2 thin film exhibited a response of 1.5 towards 50 ppm of HCHO with a fast response (32 s) and complete recovery (172 s) at its optimal temperature (250°C). In the last, the synthesis of ZnO nanomaterials using laser ablation technique was explained in detail. At recent, the synthesis of metal oxide nanomaterial without chemicals and using sophisticated equipments is big challenge in this industry. We have synthesized ZnO naoparticles and the gas sensing performance (especially HCHO) was analyzed. The fabricated devices show response to HCHO but the sensitivity (1.8 to 50 ppm of HCHO) and selectivity were poor.

In chapter 5, we explored the effect of surface decoration of laser ablated ZnO nanoparticles over SnO_2 thin film towards formaldehyde sensing by fabricating ZnO/SnO_2 n-n heterojunction based sensor. After surface decoration, the fabricated sensor was exposed by various concentration of HCHO. The results were analyzed and compared with pristine SnO_2 thin film sensor. The results reveal that after surface decoration with ZnO nanoparticles on SnO_2 thin film, a huge change in gas sensing performance was observed. The fabricated sensor exhibited a high response of 20 towards 50 ppm of HCHO at a reduced operating temperature (200°C) with a fast response (4 s) and recovery time (30 s). The sensitivity was enhanced by nanostructured/surface engineering because more reactive sites have been increased for gas molecule interaction. We also explore the effect of surface decoration via laser ablated p-type NiO nanoparticles on n-type SnO_2 thin film. In this work, p-type NiO and n-type SnO_2 formed p-n type heterojunction. Nowadays, sensitivity is not the main parameter to measure the gas

sensing performance, while selectivity is the main challenge on the commercial platform. A varying concentration of HCHO was applied to the heterojunction based sensor and it exhibited higher response (R_a/R_g) of about 31.04 towards 50 ppm HCHO at 210°C with good selectivity compared with pristine SnO_2 sensor.

In Chapter 6, the formaldehyde gas sensing mechanism has been discussed. We have discussed the effect of n or p-type metal oxide materials on n-type metal oxide via the formation of n-n or p-n heterojunction. Moreover, adsorption (K_a) and desorption rate constant (K_d), response time (τ_{res}), recovery time (τ_{rec}) and surface coverage (θ) of NiO/SnO_2 sensor were extracted from experimental data using Langmuir gas adsorption-desorption model via curve fitting method.

In conclusion, of this thesis work, we explored the formaldehyde sensing properties using laser ablated metal oxide nanoparticles on a metal oxide thin film via surface decoration method. Thus, the experimental results revealed that the laser ablation method has great potential to use as an alternative chemical free surface decoration route to fabricate metal oxide heterojunction based sensors for the detection of formaldehyde or other toxic gases. In order to validate our research, various gas sensing parameters such as sensor responses, response and recovery times, operating temperatures, selectivity etc. of our fabricated SnO_2, ZnO, ZnO/SnO_2 and NiO/SnO_2 sensors have been compared in Table 7.1.

Table 7.1: Comparison between various sensing materials used in our present work.

Sensing Material/fabrication method	Operating temperature (°C)	Response to HCHO (R_a/R_g)/concentration	Response time (τ_{res}) /Recovery time (τ_{rec})	Selectivity
Pristine SnO_2 thin film (Sputtering)	300	1.5 /50 ppm	32 s /72 s	poor
Pristine ZnO nanoparticles (Laser ablation)	350	1.8 / 50 ppm	25 s /12 s	poor
ZnO / SnO_2 (Laser ablation/Sputtering)	250	20 / 50 ppm	4 s /30 s	good
NiO / SnO_2 (Laser ablation/Sputtering)	210	31.04 /50 ppm	3 s /91 s	excellent

Accordingly, these results definitely show that the NiO NPs decorated SnO_2 gas sensor has achieved excellent sensing properties (β = 31.04 towards 50 ppm HCHO at 210°C operating temperature) compared with other nanostructured sensing materials. In addition, we also used our developed sensor to detect formaldehyde in fish samples.

7.2 Detection of formaldehyde in formalin-treated fish sample

Our objective is to develop a metal oxide based sensor to detect formaldehyde in indoor air and as well as in formalin-treated fish samples. Our fabricated SnO_2 based sensor was used for the rapid detection of formaldehyde in formalin-treated fish samples for real time state-of-the-art formaldehyde sensing applications. To evaluate the formaldehyde gas sensing capabilities of the fabricated sensors, we have prepared some formalin-treated fish specimen samples in our lab. For that purpose, we have purchased some freshly caught fresh-water fish from the local fish market, as shown in figure 7.1 (a). We have used the fillet portion of the fish sample for this verification and the fillet portion of the fish was cut into small pieces having sizes of 1 cm x 1 cm x 0.5 cm (volume = 0.5 cm^3), as shown in figure 7.1 (b). After cutting the fish into small pieces (the weight of each piece of about 5 g), they were dipped into the dilute formalin solution of 10% (v/v) as used by dishonest fish sellers. After dipping the fish samples in airtight glass bottle container (Figure 7.1 (c)) at room temperature, the samples were dipped for few hours to ensure the complete penetration of formalin solution into the fish sample (formalin solution penetration rate 0.2 mm/hour). After dipping the fish samples in formalin solution for a few hours, the samples were well rinsed several times under the continuous flow

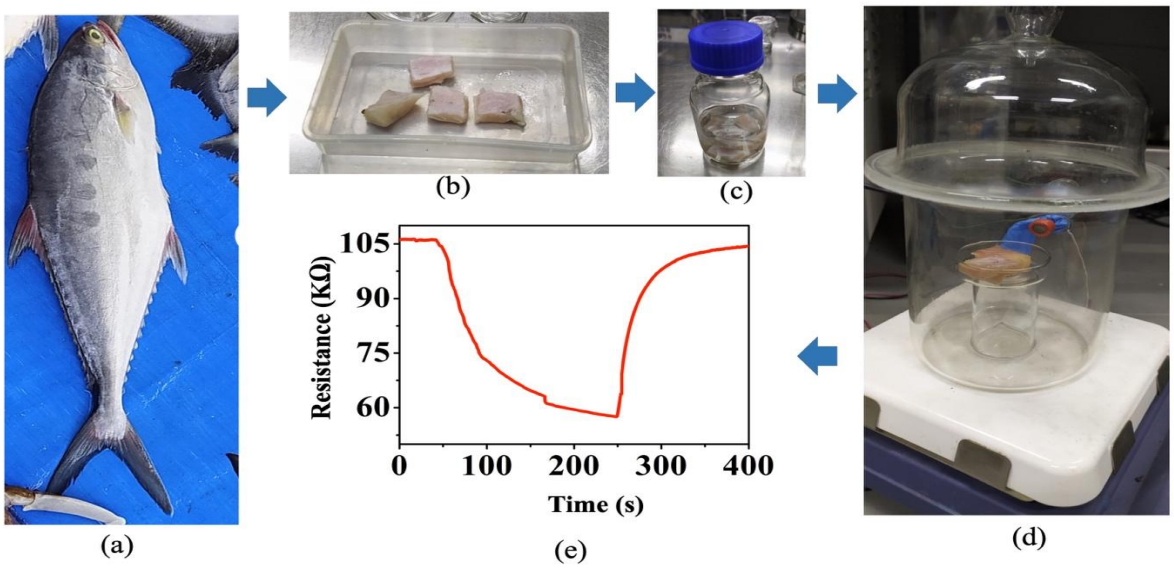

Figure 7.1: (a) Freshly caught fish. (b) Cut pieces of fish sample. (c) Dipped fish sample in 10% (v/v) formalin solution. (d) Fish sample in the glass test chamber. (e) Change in resistance of sensor due to formalin-treated fish sample.

of tap water. Next, to detect the formaldehyde gas in the formalin-treated fish sample, the samples were kept in a glass chamber (Figure 7.1 (d)) at room temperature of about 25°C and the fabricated sensor was exposed by formaldehyde VOCs emitted from the fish sample. Due to the emission of formaldehyde from the fish samples, the resistance of the sensor was reduced exponentially, as shown in figure 7.1 (e). It was also observed in figure 7.1 (e) that the sensor took long time to reach the saturation level of change in resistance due to the emission of formaldehyde gas by the off-gassing from the formalin-treated fish sample. To calculate the concentration of formaldehyde content in the fish sample, the change in resistance of the sensor was compared with the previous results (Figure 7.1 (d)). It was observed in the graph (Figure 7.1 (d)) that the change in resistance value of the sensor was matched with our previous results when the sensor was exposed by 5 ppm formaldehyde gas. The results were cross-checked by placing another fresh fish sample (without formalin-treated) in the glass chamber and the resistance value of the sensor was continuously measured after exposing the odour of the fish sample. In this last experiment, no significant change in baseline resistance was observed. However, it was deduced that in the presence of formalin-treated fish samples in the glass chamber, the change in resistance of the sensor occurred due to degassing of formaldehyde

from the fish sample. So, the fabricated sensor can be used to detect the presence of formaldehyde in formalin-treated fish samples as used by dishonest fish sellers in the market.

7.3 Future Work

Overall, despite the promising results observed during the presented studies, there is a lot of scopes and dimension that need to be explored in future. For the development of a portable formaldehyde detection system, there is a huge requirement of low power metal oxide based gas sensors with high sensitivity and good selectivity. Over the last decade, the Internet of Things (IoT) opened a new avenue for the rapid detection of formaldehyde in indoor areas and as well as the presence of formaldehyde in food (especially in fish) and to fulfil these requirements, researchers are trying to find suitable HCHO sensing material which can work with low power. So in future, simple and reliable cost-effective synthesis techniques and suitable materials should be explored to fabricate heterojunction based HCHO sensors to fulfill the need of low power for interfacing battery operated smart-systems. Figure 7.2 and 7.3 show the schematic and real-time gas monitoring system which we have developed for the detection

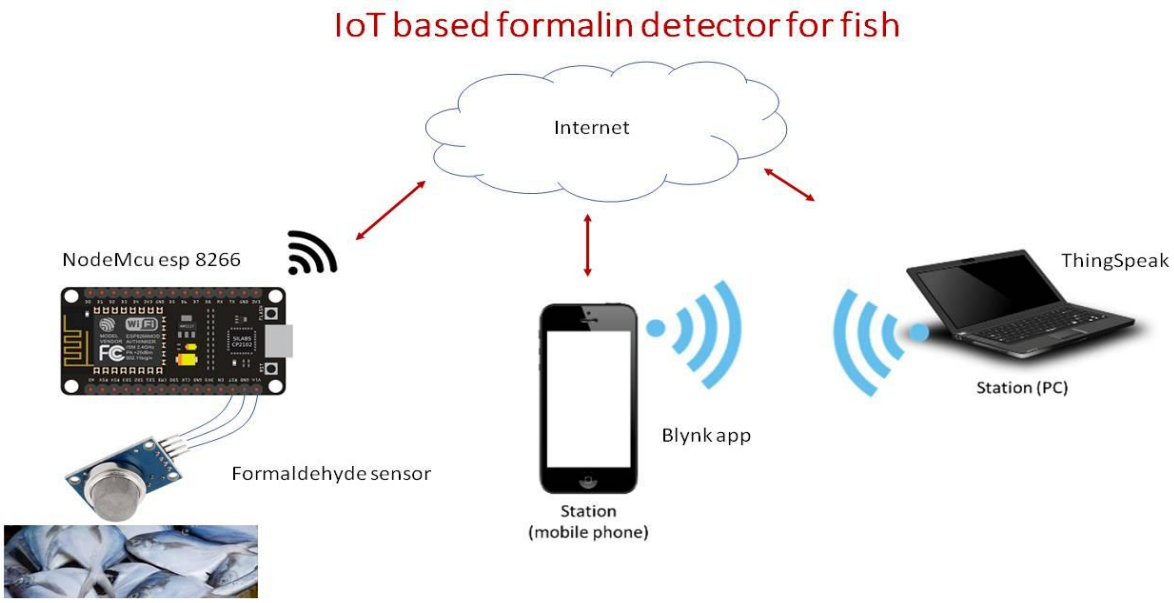

Figure 7.2 : Scematic diagram of IoT enabled smart formaldehyde detection system for fish.

of formalin in fish and formaldehyde gas in indoor air. Inttially, we have tested pristine SnO_2 based sensors (Figure 7.3) in IoT based gas monitoring system but in future, we have plan to use heterojunction based sensors (ZnO/SnO_2 and NiO/SnO_2) with IoT based system.

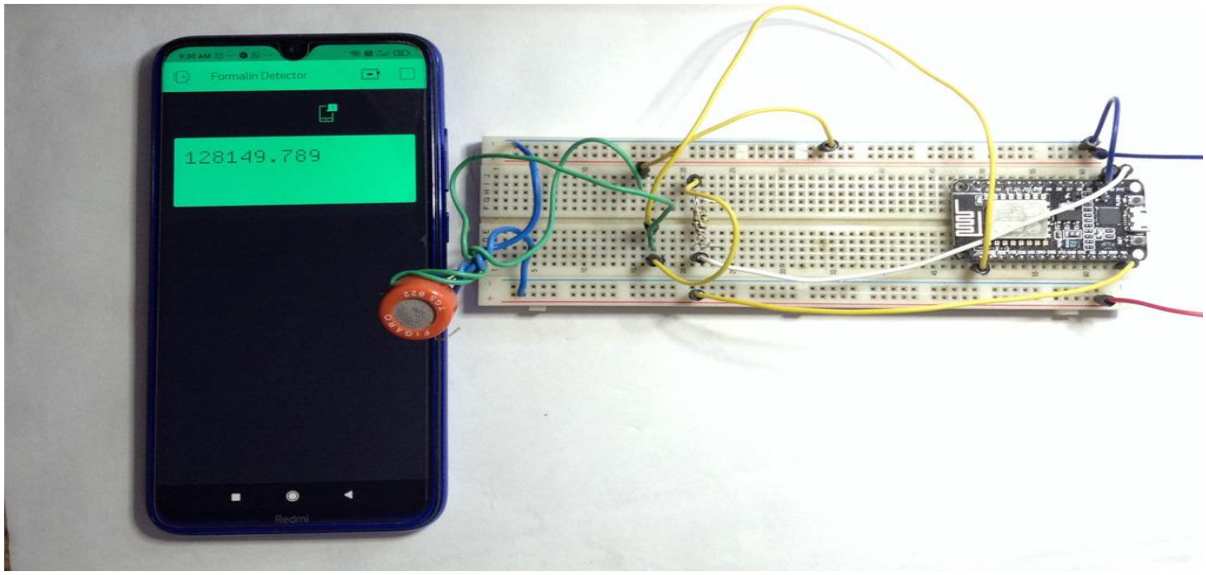

Figure 7.3 : IoT enabled formaldehyde detection system for indoor air quality monitoring system.

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