

Fabrication of LPG Sensors Based upon Chemically Tailored Sizes of Chromium Oxide Nanoparticles

Nipin Kohli¹, Onkar Singh¹, Manmeet Pal Singh², Ravi Chand Singh¹

¹ *Department of Physics, Guru Nanak Dev University, Amritsar 143005, India*

nipinkohli82@yahoo.com

² *Department of Applied Sciences, Khalsa College of Engineering & Technology, Amritsar-143001, India*

Abstract:

In this work, an attempt has been made to alter the particle size of chromium oxide and then to investigate sensing behaviour of these Cr_2O_3 samples towards LPG. We have followed chemical route for synthesizing nanoparticles of chromium oxide. To tailor nanoparticles of chromium oxide, synthesis was carried out at various reaction temperatures namely, 5, 27 and 65°C. In order to understand the structure and morphology of synthesized materials; they were subjected to X-ray diffraction and field emission scanning electron microscope. The obtained results have endorsed our prejudice and we found that reaction temperature has played a pivotal role in tailoring particle sizes. Interestingly, we observed that Cr_2O_3 nanoparticles synthesized at 27°C were smaller as compared to those synthesized at 5 and 65°C. Thick film gas sensors of thus-prepared Cr_2O_3 powders were obtained by depositing them on alumina substrates. These fabricated sensors were studied for their optimum operating temperatures for LPG and we found that all the sensors exhibited best response at 250°C. The investigation revealed that sensing response of Cr_2O_3 nanoparticles synthesized at 27°C was exceptionally higher than that of Cr_2O_3 nanoparticles synthesized at 5 and 65°C.

Key words: semiconducting, nanoparticles, sensors, LPG

Introduction

Semiconducting metal oxides have been attracting substantial interest of scientific fraternity because of their low cost, simple construction, small size and good sensing properties [1]. Chromium oxide is an interesting material and belongs to same family. It has been a widely studied material because of its wide range of applications [2-4].

In the recent past, nanoparticles have gained importance due to their unique optical, electrical, thermal and catalytic properties.

In the present study we have synthesized chromium oxide nanostructures by using chemical route. The size modification of Cr_2O_3 nanoparticles was carried out by varying the reaction temperature of precursor solution and hence its effect on sensor response towards liquefied petroleum gas (LPG) has been investigated.

Experimental Details

Synthesis of nanostructured Cr_2O_3 by precipitation method

For obtaining precipitate, we initiated with the 0.2 M solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in distilled water to which ammonia solution was added drop wise with continuous stirring. Following similar procedure, we prepared three different reaction mixtures and maintained their reaction temperature at 5, 27 and 65°C. The resulting precipitate in each case was separated from solutions, washed and dried at 120°C, and samples thus collected were calcined at 500 °C for 3 hours.

Material characterization

For crystal structure analysis, the prepared samples were characterized by powder X-ray

diffraction (XRD) using Cu K α radiation with Shimadzu 7000 Diffractometer. Morphology of the samples was analyzed by the field emission scanning electron microscope (FESEM) with FEI Quanta 200F. Brunauer–Emmett–Teller (BET) analysis was carried out to investigate the specific surface area with Gemini (V) 2380.

Fabrication of thick film sensor and sensor testing set up

To fabricate thick film sensors, a paste was prepared by mixing a proper amount of calcined powder with distilled water. The thick film of paste was then painted onto an alumina substrate (12 mm x 5 mm size) having gold electrical contacts 2 mm apart. No material as a binder was used since fine particles of chromium oxide were self binding very well. Using above procedure a batch of sensors based on powders synthesized at different reaction temperature were fabricated and cured at 350°C for 30 min.

For studying the sensing characteristics, a simple home built apparatus was used which consists of a simple potentiometric arrangement, a test chamber of 40 liters volume in which a sample holder, a small temperature controlled (by dimmer stat & thermocouple) oven and a mixing fan were installed. The fabricated sensor was placed in the test chamber oven at suitable temperature, and known quantity of gas species was injected into the test chamber. Variation of real time voltage signal across a resistance connected in series with sensor was monitored and recorded was recorded with an experimental set up consisting of Keithley Data Acquisition Module KUSB-3100 and a computer. All the sensors were tested following same procedure by varying temperature from 200 to 400°C.

Results and discussion

Structural analysis

Fig. 1 represents the X-ray diffraction pattern of materials synthesized at various reaction temperatures. The peaks visible in the graphs are in well agreement with standard available data, and these depict the corundum structure of nanosized chromium oxide. The crystallite size of chromium oxide powder synthesized at 5, 27 and 65°C was found to be 42.6, 20.5 and 30.2 nm as determined by using Scherrer's formula.

Fig. 2(a)–(c) represents the FESEM images of the nanostructured Cr₂O₃ powders at various

reaction temperatures. Some clusters and agglomeration are also seen in the pictures.

The values obtained for the BET surface area are 13.9135, 29.3875 and 26.803 m²/g for the nanoparticles synthesized at 5, 27 and 65°C respectively.

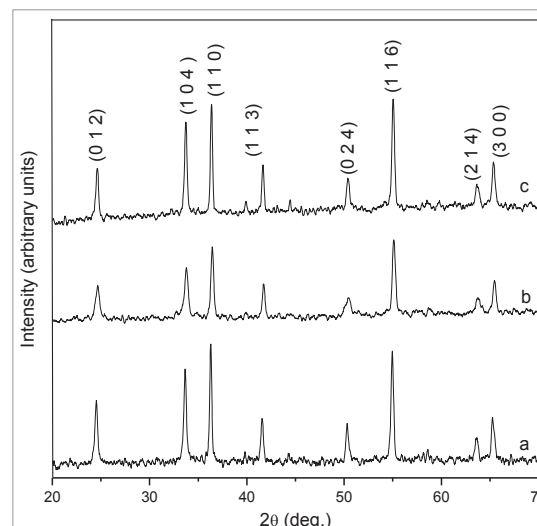
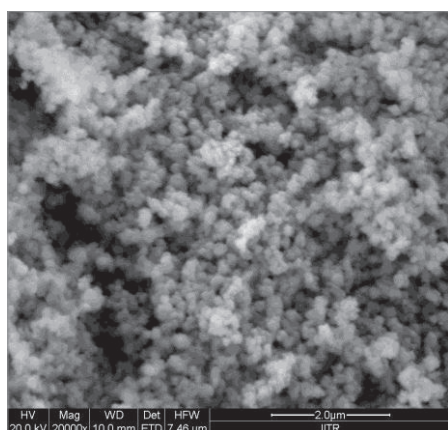


Fig. 1. XRD patterns of Cr₂O₃ powder synthesized at (a) 5°C, (b) 27°C and (c) 65°C.

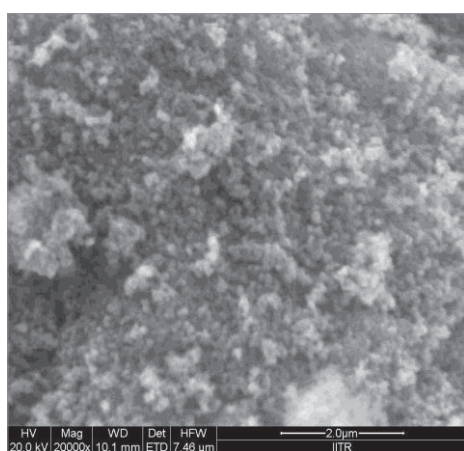
Both hydrolysis and supersaturation are strongly dependent on reaction temperature. When the temperature is lowered from 27° to 5°C, slow hydrolysis reaction takes place which in turn leads to larger sized particles. Increase in temperature from 27° to 65°C results in increased solubility and thus a reduced supersaturation of growth species in the solution. As a result, nuclei with small sizes may become unstable and dissolve back into the solution; dissolved species will then deposit onto the surfaces of large particles. This dissolution-growth process is also known as Ostwald ripening in which large particles grow at the expense of small particles [5].

Sensing performance

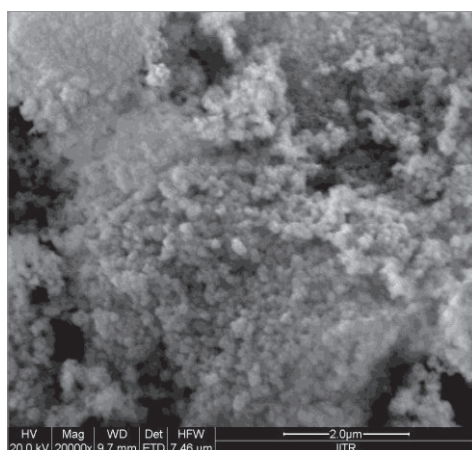
Sensors fabricated from powder synthesized at different reaction temperatures were exposed to 500 ppm liquefied petroleum gas at different temperatures and results are shown in Fig. 3. Study revealed that optimum operating temperature of all the sensors remained invariant at 250°C.



(a)



(b)



(c)

Fig. 2. FESEM micrographs of Cr_2O_3 powder synthesized at (a) 5°C , (b) 27°C and (c) 65°C .

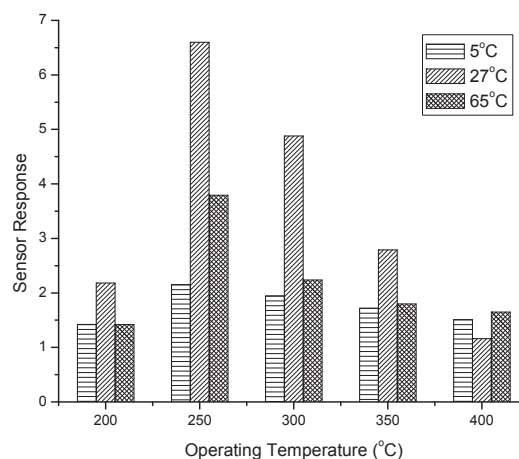
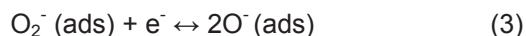


Fig.3. Sensing response of chromium oxide nanoparticles synthesized at 5, 27 and 65°C towards 500 ppm of LPG at various operating temperatures.

It is also evident from the same figure that sensing response is exceptionally higher for the sample synthesized at 27°C as compared to samples synthesized at other reaction temperatures (5 and 65°C). The sensors fabricated from powder synthesized at pH 11 were exposed to 500 ppm LPG at 250°C and the variation of sensor response with time is given in Fig. 4. Exceptionally higher sensing response of samples synthesized at temperature 27°C may be attributed to the smaller grain size obtained at this temperature. Another reason for enhanced sensing response of nanoparticles synthesized at 27°C is the larger effective surface area of smaller sized nanoparticles. Also a large number of small particles can be accommodated on a unit surface area contributing to large number of active sites onto which gaseous species adsorb to initiate sensing process.

When Cr_2O_3 based nanostructured sensors are exposed to air, oxygen molecules get adsorbed on the surface of the materials to form O_2^- , O^- , O^{2-} ions by capturing electrons, thereby removing holes from the valence band. As a result, conductance of sensors decreases. The reaction kinetics is given in eqs.(1-3).



When reducing gas such as LPG is injected into the test chamber, it reacts with the adsorbed

oxygen resulting in the decrease in conductance. Therefore with reducing gas on this p-type sensor, the conductivity drops. Upon removal of reducing species or introduction of air or oxygen, the mechanism is reversed and the conductivity returns to its original state.

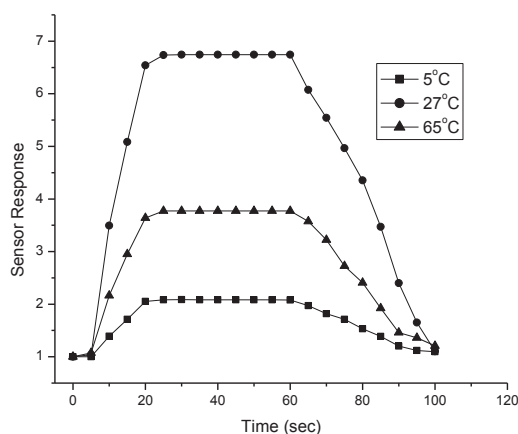


Fig. 4. Sensing characteristics of sensors fabricated from material synthesized at 5, 27 and 65°C exposed to 500 ppm LPG at 250°C.

Conclusions

Chromium oxide nanoparticles have been synthesized using precipitation technique at different reaction temperatures. It was found that reaction temperature has played a pivotal role in tailoring particle sizes. Interestingly, we observed that Cr_2O_3 nanoparticles synthesized at 27°C were smaller as compared to those synthesized at 5 and 65°C. Sensing response of synthesized powders was investigated for LPG and it was observed that sensor fabricated from powder synthesized at 27°C shows best response due to small crystallite size.

Acknowledgements

Authors would like to thank the following: University Grants Commission, New Delhi for financial support; SAIF, All India Institute of Medical Sciences, New Delhi for TEM investigations; Dr. S. A. Hashmi, Department of Physics and Astrophysics, University of Delhi for BET investigations.

References

- [1] S. R. Morrison, Mechanism of semiconductor gas sensor operation, *Sensors and Actuators B* 11, 283-287 (1987); doi: 10.1016/0250-874(87)80007-0
- [2] Y. Takeda, R. Kanno, Y. Tsuji, O. Yamamoto, H. Taguchi, Chromium oxides as cathodes for lithium cells, *Journal of Power Sources* 9, 325-328 (1983); doi: 10.1016/0378-7753(83)87034-7
- [3] D.N. Suryawanshi, D.R. Patil, L.A. Patil, Fe_2O_3 -activated Cr_2O_3 thick films as temperature dependent gas sensors, *Sensors and Actuators B* 134, 579-584 (2008); doi: 10.1016/j.snb.2008.05.045
- [4] Y. Liu, D.Y. Chen, Protective coatings for Cr_2O_3 -forming interconnects of solid oxide fuel cells, *International Journal of Hydrogen Energy* 34, 1-7 (2009); doi: 10.1016/j.ijhydene.2009.09.022
- [5] G. Cao, Nanostructures and Nanomaterials: Synthesis, Properties & Applications 1st ed., Imperial College Press, London.