Chapter 5

Sensing Behaviour of Chromium Oxide Nanostructures Synthesized at Various Reaction Temperatures

5.1 Introduction

In the previous chapter the effect of pH on the particle size of chromium oxide nanoparticles and their properties was studied. However, there are other parameters which control the particle size and particle–size distribution. The successful chemical synthesis of nanocrystals involves three steps: nucleation, growth and termination by the capping agent or ligand. Though the reaction temperature and reagent concentrations provide a rudimentary control of the three steps, it is often impossible to independently control them and therefore obtained nanocrystals usually exhibit a distribution in size (Kulkarni et al. (2004)). In this chapter, an attempt has been made to control the particle size by varying the reaction temperature.

Singh et al. (2008) reported that increase in reaction temperature results in change in morphology of ZnO nanostructures. Qu et al. (2006) studied the effect

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5. Sensing Behaviour of Chromium Oxide Nanostructures Synthesized at Various Reaction Temperatures

of reaction temperature on the particle size, structure and magnetic properties of co–precipitated CoFe$_2$O$_4$ nanoparticles and observed that the average size of nanoparticles increases with the increase in reaction temperature. Hakuta et al. (2005) prepared γ–AlO(OH) by using hydrothermal process and found that the particle size increased with an increase in the reaction temperature. Zhang et al. (2007) studied the influence of reaction temperature on the shape and size distribution of Cu$_2$O nanoparticles and observed that average size of the Cu$_2$O nanoparticles was decreased and the size uniformity of the nanoparticles was improved with increasing temperature. Kim et al. (2010) have controlled the crystal structure and crystallite morphology of 1D nanostructured manganese oxides by tuning of reaction temperature.

5.2 Synthesis of chromium oxide nanoparticles at different reaction temperatures

Nanoparticles of chromium oxide were prepared by following a precipitation technique as discussed in Chapter 4. I started with a 0.2 M aqueous solution of CrCl$_3$·6H$_2$O in distilled water to which ammonia water was added to obtain the precipitate. Following similar procedure, three different reaction mixtures were prepared by keeping the pH same in each case and maintained their reaction temperature at 5, 27 and 65$^\circ$C. The precipitate thus obtained was filtered, washed and dried into powder at 120$^\circ$C. The samples thus obtained were calcined at 500$^\circ$C for 3 hours.

The crystal structure of the materials produced was characterized by powder X–ray diffraction (XRD) using Cu K$_\alpha$ radiation with Shimadzu 7000 Diffractometer system. Size and morphology of material particles were analyzed by transmission electron microscope (TEM) with Morgagni 268 operating at 80 kV and field emission scanning electron microscope (FESEM) with Carl Zeiss Supra 55. Brunauer–Emmett–Teller (BET) analysis was carried out to investigate the specific surface area with Gemini (V) 2380.

5.3 Sensor fabrication and testing method

Using technique explained in Chapter 2, a batch of sensors based on samples synthesized at different reaction temperatures were fabricated and cured at 350$^\circ$C.
for 30 min. All the sensors were tested following same procedure by varying temperature from 200 to 400°C.

5.4 Results and Discussion

5.4.1 Structural Analysis

X-ray diffraction plots of chromium oxide powder prepared at different reaction temperatures are shown in Fig. 5.1. The diffraction patterns in all the plots are in agreement with the standard X-ray diffraction peaks, which confirmed that the synthesized materials were Cr$_2$O$_3$ of corundum structure.

![XRD patterns of Cr$_2$O$_3$ powder synthesized at different temperatures](image)

**Figure 5.1**: XRD patterns of Cr$_2$O$_3$ powder synthesized at (a) 5°C, (b) 27°C and (c) 65°C.
5.4 Results and Discussion

Figures 5.2–5.4 show FESEM micrographs of chromium oxide powder prepared at different reaction temperatures. From these images it is clear that rod like structure is formed at 5°C but at 27 and 65°C the formation of nanoparticles is seen.

Figure 5.2: FESEM micrograph of $\text{Cr}_2\text{O}_3$ powder synthesized 5°C.
5.4 Results and Discussion

Figure 5.3: FESEM micrograph of Cr$_2$O$_3$ powder synthesized 27$^\circ$C.

Figure 5.4: FESEM micrograph of Cr$_2$O$_3$ powder synthesized at 65$^\circ$C.
Figures 5.5–5.7 represent TEM images of chromium oxide powder prepared at different reaction temperatures. Figures 5.8–5.9 represent distribution histograms corresponding to TEM images of chromium oxide powder prepared at 27 and 65°C. It is quite evident from distribution histograms that synthesis of material at reaction temperature 27°C yielded smaller sized Cr$_2$O$_3$ particles as compared to particles obtained at 65°C. The values obtained for the BET surface area are 13.9135, 29.3875 and 26.803 m$^2$/g for the nanostructures synthesized at 5, 27 and 65°C respectively.

**Figure 5.5:** TEM micrograph of Cr$_2$O$_3$ powder synthesized at 5°C.
Figure 5.6: TEM micrograph of $\text{Cr}_2\text{O}_3$ powder synthesized at 27°C.

Figure 5.7: TEM micrograph of $\text{Cr}_2\text{O}_3$ powder synthesized 65°C.
5.4 Results and Discussion

Figure 5.8: Distribution histogram of TEM image of Cr$_2$O$_3$ powder synthesized at 27°C.

Figure 5.9: Distribution histogram of TEM image of Cr$_2$O$_3$ powder synthesized at 65°C.
During the synthesis of material, a supersaturated solution possesses a high Gibbs free energy. The driving force for the processes of crystallization (i.e. nucleation, precipitation, growth, deposition, etc.) is the difference in the free energy of supersaturated phase and the free energy of the newly forming phase. Under constant temperature and pressure conditions, any change in a system proceeds from a state of higher to a state of lower Gibbs free energy. Change in Gibbs free energy can be significantly increased by increasing the supersaturation for a system (Cao (2004)).

Various factors such as supersaturation, nucleation and growth rate, colloidal stability, recrystallization and aging process influence the particle morphology. Generally, supersaturation, which is highly dependent on the solution temperature, has a predominant influence on the morphology of the precipitate. A highly supersaturated solution possesses high Gibbs free energy. Now formation of one-dimensional nanostructure requires anisotropic growth of material, i.e. the crystal should grow along a certain orientation faster than the other directions. The anisotropic growth takes place at low supersaturation (Cao (2004)). Eventually at low temperature suitable conditions are met, resulting in the synthesis of Cr$_2$O$_3$ nanorods. As the temperature is increased to 27°C, a fast hydrolysis reaction takes place resulting in the high supersaturation, which in turn leads to the formation of a large number of small nuclei. Further increase in the temperature to 65°C results in an increased solubility, and thus a reduced supersaturation of growth species in the solution. As a result, nuclei with small size 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 (Cao (2004)).

### 5.4.2 Sensing Characteristics

Sensors fabricated from powder synthesized at different reaction temperatures were exposed to 250 ppm of ethanol vapour at different operating temperatures and results are shown in Fig. 5.10. It is quite clear from this figure that optimum operable temperature for all the samples is same and lies at 250°C.

The sensors fabricated from powder synthesized at 5, 27 and 65°C were exposed to 250 ppm ethanol vapour at 250°C and their sensing response is shown in Fig. 5.11. It is evident from Fig. 5.10 and 5.11 that sensing response is exceptionally higher for the sample synthesized at 27°C as compared to those synthesized...
5. Sensing Behaviour of Chromium Oxide Nanostructures Synthesized at Various Reaction Temperatures

at 5 and 65°C. Exceptionally higher sensing response of samples synthesized at temperature 27°C may be attributed to the smaller grain size obtained at this temperature. At low temperature i.e. 5°C, sensing response decreases due to the formation of nanorods having low surface to volume ratio. As the temperature is increased to 65°C, the decrease in sensor response is observed because of the increase in particle size. At 27°C due to smaller particle size, 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. Figure 5.12 represents sensing response of sample synthesized at 5, 27 and 65°C as a function of vapour concentration at 250°C, which is almost linear up to 700 ppm concentration.
Figure 5.10: Sensing response towards 250 ppm ethanol for the samples synthesized at different reaction temperatures at different operating temperatures.
Figure 5.11: Sensing characteristics of sensors fabricated from material synthesized at 5, 27 and 65°C exposed to 250 ppm ethanol at 250°C.
Figure 5.12: Variation of sensor response to ethanol as a function of vapour concentration at 250°C for the samples synthesized at 5, 27 and 65°C.
5.5 Conclusion

Chromium oxide nanoparticles have been synthesized using precipitation technique at different reaction temperatures. The reaction temperature played an important role in controlling the morphology and particle size during synthesis process. Nanorods were obtained at 5°C, and at 27 and 65°C formation of particles takes place. Sensing response of synthesized powders was investigated for ethanol and it was observed that sensor fabricated from powder synthesized at 27°C shows best response due to small particle size and greater surface to volume ratio as compared to nanoparticles synthesized at 65°C and nanorods synthesized at 5°C.
5. Sensing Behaviour of Chromium Oxide Nanostructures
Synthesized at Various Reaction Temperatures