Synthesis, Morphological, and Elemental Analysis of Pure and Tin Doped Chromium Oxide Nanoparticles

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Abstract

Objectives: To synthesize the pure and tin doped chromium oxide nanoparticles and analyzing the structural, morphological, and elemental composition of the prepared samples. Methods: Sn$^{2+}$ doped chromium oxide (Cr$_2$O$_3$) nanoparticles are synthesized by microwave-assisted solvothermal method which is simple and cost effective. The pure as prepared sample was subjected to TG/DTA analysis. The impact of the added dopant (Sn$^{2+}$) on the Cr$_2$O$_3$ nanoparticles was investigated by X-ray diffraction pattern, scanning electron microscopy, and Energy dispersive X-ray spectra. Findings/application: The synthesized tin doped chromium oxide nanoparticles were annealed at 700 °C for 2 h to enhance the crystalline quality and to obtain the desirable crystal phase. The annealed samples were found to be in rhombohedral structure and its average grain size decreases from 24 to 10 nm on increasing the dopant concentration. The scanning electron micrograph corroborates that the prepared nanoparticles are mostly spherical in shape. The Energy dispersive X-ray spectra ensure the presence of Cr, O, and Sn. This study has proven that the particle size will be tuned by increasing the concentration of Sn$^{2+}$ in pure Cr$_2$O$_3$ nanoparticles. The Cr$_2$O$_3$ nanoparticles are mainly used in paints and pigments, the reduction in size increases the coating performance such as scratch resistance, hardness, and UV resistance.

Keywords: Chromium Oxide, Solvothermal Method, X-ray Diffraction Pattern, Scanning Electron Microscopy, Rhombohedral, Energy Dispersive X-ray Spectra.

1. Introduction

Nano-structured materials [1–2] have attracted many researchers in recent times due to their unique physical and chemical properties in contrast to the bulk counterpart. High surface area, high density of edge surface sites, and the limited size of the nanosized...
materials [3–4] make them suitable in different potential applications. Among inorganic nanoparticles, chromium (III) oxide (Cr$_2$O$_3$) nanoparticles have impressed the researchers due to its myriad uses in developing nano pigments [5], heterogeneous catalysts [6–8] coating and wear resistive materials [9–10], hydrogen storage [11–13], digital recording system, photonic and electronic devices [14–15]. Several crystalline structures of chromium oxides like, corundum (Cr$_2$O$_3$), rutile (CrO$_2$), CrO$_3$, CrO$_4$, Cr$_2$O$_5$, and Cr$_3$O$_{12}$ has been reported in literatures [16]. Various methods have been developed by several researchers for the synthesis of Cr$_2$O$_3$ nanoparticles such as precipitation method [17–19], solvent free method [20], hydrothermal synthesis [21–22], solvothermal method [23–24], thermal decomposition method [25–26], sol gel method [27–29], and sonochemical method [30]. Though many researchers have adopted different techniques to produce Cr$_2$O$_3$ nanoparticles, here we dealt with the simple and cost effective microwave-assisted solvothermal method to synthesize chromium oxide (Cr$_2$O$_3$) nanoparticles which significantly reduces the reaction time from hours to minutes. Ethylene glycol is used as a solvent as it lowers the particle size and act as a good reducing agent. The influence of Sn$^{2+}$ on the structural and morphological features of the pure Cr$_2$O$_3$ nanoparticles has been explored. The structural and morphological study of pure and doped Cr$_2$O$_3$ nanoparticles play a vital part in exploiting the properties for their use in several emerging technologies.

2. Materials and Methods

Chromium triacetate (Cr(C$_2$H$_3$O$_2$)$_3$), urea (H$_2$NCONH$_2$), stannous chloride dehydrate (SnCl$_2$·2H$_2$O) were used as the precursor and ethylene glycol was used as solvent. Distilled water and acetone was used for washing the samples. Initially, chromium acetate and urea were taken in the molecular ratio 1:3 and dissolved in 200 ml ethylene glycol then it was stirred well with the help of a magnetic stirrer. The dissolved solution should be kept under microwave irradiation until the solvent evaporated completely. The resulting colloidal particles were washed several times with water and then with acetone to remove the impurities if present. Then the samples were dried in atmospheric air at room temperature. The dried samples were annealed at 700 °C for 2 h and collected as yield. Similar procedure was carried out for the preparation of Sn$^{2+}$ doped Cr$_2$O$_3$ nanoparticles by adding different concentration of dopants (2, 4, 6, 8, and 10 wt%) with the above precursors used to prepare the pure samples. The prepared samples were structurally characterized by X’Pert Pro-PAnalytic diffractometer with monochromated CuKα radiation (wavelength 1.5406 Å). The morphology of the pure and Sn$^{2+}$ doped samples have been unveiled with SEM images obtained from scanning electron microscopy (Jeol, Japan). The atomic weight percentage of the elements found in the pure and Sn$^{2+}$ doped samples were obtained from EDX spectra recorded by Oxford instruments, UK.

3. Results and Discussion

3.1. TG/DTA Analysis

The as prepared sample of pure Cr$_2$O$_3$ was subjected to TG/DTA analysis in order to study its thermal stability which is the pre-requirement for device application. The differential
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The thermal and thermogravimetric curves obtained for the as prepared Cr$_2$O$_3$ nanorods are shown in Figure 1.

The TG/DTA measurement was performed under nitrogen (inert) atmosphere in the temperature range 30–900 °C. Four steps of weight loss were noticed in TG curve. The first step happened below 100 °C with a weight loss of 10 wt% was attributed to the removal of absorbed water. The second step between 100 and 270 °C with a weight loss of 26.2 wt% was brought about by the deterioration of Cr(OH)$_3$, and in the third step the huge weight loss acquires due to decomposition of oxygen. From the TG/DTA analysis, it is confirmed that the samples are highly in a single phase of Cr$_2$O$_3$ above 500 °C. Therefore, in order to improve the crystallinity and purity of sample phase, all the prepared samples were annealed at the temperature of 700 °C for 2 h and further used for all measurements.

3.2. PXRD Analysis

The PXRD pattern of pure and doped Cr$_2$O$_3$ nanoparticles is shown in Figure 2. The peaks were marked by comparing the reported JCPDS data file no 82-1484. It belongs to rhombohedral system with lattice parameter a = 4.957Å; c = 13.592Å and space group $R\bar{3}c$. The indexed diffraction pattern clearly indicates that the increase in dopant concentration gradually reduces the peak intensity and increases full width half maximum (FWHM). The reason is that the restrained amount of Sn$^{2+}$ atoms entered as substitutes sharing the oxygen with Cr atoms and hence diminishes the crystallinity [31–32]. A slight move towards the lower degree which is seen in the Sn$^{2+}$ doped samples may due to the difference between ionic radii of the substitutes Sn$^{2+}$ (1.18 Å) with that of Cr$^{3+}$ (0.64 Å).

Table 1 shows the lattice parameters (a&c) of the pure and Sn$^{2+}$ doped Cr$_2$O$_3$ nanoparticles calculated from the equation [33],

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a^2}\right] + \frac{l^2}{c^2}$$

where d is the interplanar distance and h, k, l are the Miller indices of the plane.
The variation of the lattice parameters on increasing the dopant concentration revealed that added dopant has successfully entered in Cr$_2$O$_3$ lattice and produce lattice elongation.

The grain size (D) has been calculated using Debye–Scherrer formula (\( D = \frac{K\lambda}{\beta \cos \theta} \)) and tabulated in Table 1.

### 3.3. SEM Analysis

In the present investigation, the morphology of pure and Sn$^{2+}$ doped Cr$_2$O$_3$ nanoparticles were unveiled with SEM. The SEM micrographs were recorded and portrayed in Figures 3–8.

**FIGURE 2.** PXRD pattern of pure and Sn$^{2+}$ doped Cr$_2$O$_3$ nanoparticles.

**TABLE 1.** Structural data of pure and doped Cr$_2$O$_3$ nano particles

| Sample name    | Dopant concentration (Wt%) | Lattice parameter (Å) | Unit cell volume | Grain size (error~ ±2) nm |
|----------------|-----------------------------|-----------------------|------------------|--------------------------|
| Pure Cr$_2$O$_3$ |                             |                       |                  |                          |
|                |                             | \( a \)               | \( c \)          |                          |
| Cr$_2$O$_3$: Sn$^{2+}$ | 2                            | 4.9573                | 13.6138          | 334.5567                 | 24           |
|                | 4                            | 4.9722                | 13.6312          | 337.0011                 | 21           |
|                | 6                            | 4.9836                | 13.6412          | 338.7965                 | 15           |
|                | 8                            | 4.9921                | 13.6533          | 340.2547                 | 13           |
|                | 10                           | 4.9984                | 13.6616          | 341.3214                 | 10           |
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**FIGURE 3.** SEM topograph of pure Cr$_2$O$_3$ NPs.

**FIGURE 4.** 2 wt% Sn$^{2+}$ doped Cr$_2$O$_3$ NPs.

**FIGURE 5.** 4 wt% Sn$^{2+}$ doped Cr$_2$O$_3$ NPs.
FIGURE 6. 6 wt% Sn$^{2+}$ doped Cr$_2$O$_3$ NPs.

FIGURE 7. 8 wt% Sn$^{2+}$ doped Cr$_2$O$_3$ NPs.

FIGURE 8. 10 wt% Sn$^{2+}$ doped Cr$_2$O$_3$ NPs.
The spherical nanoparticles were agglomerated to reduce the complete surface free vitality. It was noted that the agglomeration increases with the increasing concentration of the dopant. Because of their high surface energy the smaller nanoparticles frequently stuck to the neighboring particles, thus seemed like greater particles [34].

3.4. EDX Analysis

The elemental composition of pure and Sn$^{2+}$ doped Cr$_2$O$_3$ nanoparticles were studied using EDX analyses. The presence of Cr, O, and Sn$^{2+}$ was clearly indicated in EDX spectra shown in Figures 9–14 and the elemental proportions were tabulated in Table 2.

**FIGURE 9.** EDX spectrum of pure Cr$_2$O$_3$ NPs.

**FIGURE 10.** 2 wt% Sn$^{2+}$ doped Cr$_2$O$_3$ NPs.
FIGURE 11. 4 wt% Sn$^{2+}$ doped Cr$_2$O$_3$ NPs.

FIGURE 12. 6 wt% Sn$^{2+}$ doped Cr$_2$O$_3$ NPs.

FIGURE 13. 8 wt% Sn$^{2+}$ doped Cr$_2$O$_3$ NPs.
The atomic percentage of Cr and O for pure sample matched well with that of stoichiometric composition of Cr$_2$O$_3$ which clearly indicates the purity of the sample. The peaks due to carbon around 0.27 keV are assigned to the carbon coating layer onto the grid that make up the support on which the samples are placed. The gold peak is formed around 2.2 keV since it is used as a coating material to enhance the conductivity and to improve the resolution.

### 4. Conclusion

Pure and Sn$^{2+}$ doped Cr$_2$O$_3$ nanoparticles were prepared fruitfully by microwave-assisted solvothermal method and its annealing temperature was fixed from thermogravimetric analysis. It was proved that adding Sn$^{2+}$ with pure Cr$_2$O$_3$ nanoparticles reduces the particle size drastically. Almost spherical and agglomerated particles were identified with SEM micrograph. The EDX spectra result confirms the presence of the expected element and its atomic weight percentage.
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