Synthesis, FTIR Studies and Optical Properties of Aluminium Doped Chromium Oxide Nanoparticles by Microwave Irradiation at Different Concentrations

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Abstract In this exposure, pure and aluminium (Al) doped chromium (III) oxide (Cr_2O_3) nanoparticles are synthesized by simple solvothermal microwave irradiation (SMI) technique. SMI technique is simple and low cost; it has the future to be produced on a huge scale. The effect of dopant (Al) concentration on the structural behavior of Cr_2O_3 nanoparticles was examined by X-ray diffraction. The average crystallite size of the synthesized nanoparticles was measured from XRD patterns using Scherrer equation and was decreased from 14.56 nm to 10.86 nm with the increasing Al concentration in Cr_2O_3 from 0 to 5% (in steps of 0, 1, 2, 3, 5). Morphologies and compositional elements of the synthesized nanoparticles were observed by the field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) spectroscopy, respectively. The optical property of the samples was measured by ultraviolet - visible (UV-Vis.) absorption spectroscopy. The observed optical band gap value ranges from 2.12 eV to 1.90 eV for Al doped nanoparticles and was red shifted in comparison with that of the pure Cr_2O_3 (3.483 eV).

Keywords Cr_2O_3 Nanoparticles, SMI Method, Structural Properties, Optical Properties

1. Introduction

Nanotechnology is a branch of science which is meant to understand the fundamental physical and chemical properties and the phenomenon of nanomaterials and nanostructures and because of novel application of nanomaterials [1, 2]. The application of nanomaterials utilizes not only chemical composition but also the size, shape and surface dependent properties [3]. Nanoparticles can be noncrystalline, polycrystalline or single crystalline and can be produced

with a variety of methods [4]. For the past years, enormous progress in the properties of nanoparticles has been achieved. Nanomaterials, especially transition metal oxides play a specific role in the areas of physics, materials science and chemistry [5]. Synthesis of nanomaterials with desired morphology and composition is the most challenging task in the field of nanotechnology. The synthesis of metal oxides nanostructures have stimulated the great interest because of their novel properties which offers intensive research efforts to fabricate the efficient miniaturized devices for the applications in various nanoelectronics and photonics [6, 7, 8]. Mostly metal oxides as nanoparticles can exhibit unique chemical properties due to their limited size and high density of corner or edge surface sites [9]. Chromium (III) oxide (Cr_2O_3) nanoparticles have received special attention than the other metal oxide nanomaterials, because of multiple applications including green pigments [10], heterogeneous catalyst [11-13], coating materials for thermal properties [14, 15], solar energy collector [16] digital recording system [17]. Because of the high energy density and high capacity at low discharge rates, chromium oxides have been attracted special attention used as cathode materials [18]. A variety of fabrication techniques have been explored in the literature for the synthesis of these metal oxide nanostructures but typically, they can be divided into two categories [19]. Metal oxide nanoparticles are considered to have the potency to generate reactive oxygen species. Band structure is the fundamental material property that controls ROS - producing ability, band turning via introduction of dopants [20]. Meanwhile, doping with selective elements to metal oxides offers an effective method to enhance and control the electrical and optical properties of metal oxide structures [21]. A number of chemical methods of synthesis have been applied to synthesis Cr_2O_3 powders, for example hydrothermal [22], thermal decomposition [23].

As per green chemistry principles water as an inexpensive,

non-toxic, non-flammable and abundant material in nature, is a safer and ideal solvent for microwave - activated reactions [24-25].

In our study, pure and Al doped Cr_2O_3 nanoparticles are synthesized under microwave irradiation using triethanolamine as template and water as a green solvent aqueous solution of Aluminium nitrate is used in different concentration at different temperatures to study the effect of concentration in the synthesis of doped nano particles. Synthesis of Al doped Cr_2O_3 nanoparticles via the microwave irradiation could be worthwhile investigating.

In this paper, we report synthesis of pure Cr_2O_3 and Al doped Cr_2O_3 nanoparticles by microwave irradiation and its characterization by means of X-ray diffraction (XRD), scanning electron microscope (SEM), UV-Vis and FTIR spectroscopic methods which will give much valuable information about these materials.

2. Materials and Methods: Experimental Procedure

Synthesis of Pure Cr_2O_3 Nanoparticles

25ml of $\text{Cr}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (0.2M) aqueous solution was mixed with appropriate amount of triethanolamine as template (5 ml). After stirring for 30-40 minutes, the mixture was placed under microwave irradiation for 4 minutes. The green solid product was filtered and dried in air at room temperature. The materials were calcinated in electronic oven at 200°C , for 1 hour followed by annealing at 500°C , 700°C and 900°C .

Synthesis of Al doped Cr_2O_3 Nano Particles

Aqueous solution of $\text{Cr}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ (0.2M) was mixed with aqueous solution of aluminium nitrate $\text{Al}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ and appropriate amount of triethanolamine as template (5 ml). After stirring for 30-40 minutes, the mixture was placed under microwave irradiation for 4-7 minutes. The green solid product was filtered and dried in air at room temperature. The materials were calcinated in electronic oven at 200°C , for 1 hour followed by annealing. 99% of aqueous solution

of chromium nitrate and 1% of aluminium nitrate yielded 1% Al doped Cr_2O_3 nanoparticles. 98% of aqueous solution of chromium nitrate and 2% of aluminium nitrate yielded 2% Al doped Cr_2O_3 nanoparticles. 97% of aqueous solution of chromium nitrate and 3% of aluminium nitrate yielded 3% Al doped Cr_2O_3 nanoparticles. 95% of aqueous solution of chromium nitrate and 5% of aluminium nitrate yielded 5% Al doped Cr_2O_3 nanoparticles.

3. Results and Discussion

X-ray Diffraction Analysis

X-ray diffraction (XRD) patterns were collected with an Goniometer 3000 powder X-ray diffractometer using $\text{Cu K}\alpha$ radiation source ($\lambda = 1.540598 \text{ \AA}$), germanium crystal monochromator, at room temperature 25°C , curved position sensitive detector operating at 30 kV and 30 mA. Powder samples were loaded into a sample holder, and each pattern was collected for up to 2 h to obtain sufficiently high signal-to-noise ratio.

Figure 1 shows the XRD pattern of pure Cr_2O_3 nanoparticles prepared by $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the chromium source after annealing at 900°C . Based on the XRD pattern, whereas the prepared sample calcined at 200°C proved to be amorphous. The crystallinity of the sample annealed at 900°C was found to be much better than that annealed at 500°C or 700°C . The average crystallite sizes (D) was calculated using well known Scherrer's equation

$$D = 0.9\lambda / (\beta \cos \theta)$$

where λ , is the x-ray wavelength used in xrd ($1.540 \text{ \AA}$), β and θ are the full width at half maxima (FWHM) of the diffraction peak and the Bragg's diffraction angle respectively. The calculated average crystal size of pure (undoped) Cr_2O_3 nanoparticles using the above formula based on Table 1 was 14.56 nm and it was compared with previous studies reported as 14.82 nm [26]. The x-ray diffraction plots of 1%, 2%, 3%, 5% Al doped Cr_2O_3 are shown in figures 2-5. The crystal average size of aluminium doped Cr_2O_3 nanoparticles were calculated based on the Tables 2-5.

Table 1. Peak list with their relative intensity of XRD of pure Cr_2O_3

Pos. [$^\circ 2\theta$.]	Height [cts]	FWHM Left [$^\circ 2\theta$.]	d-spacing [$\text{\AA}$]	Rel. Int. [%]
24.51(1)	60(8)	0.20(4)	3.62868	55.75
33.602(7)	82(7)	0.21(2)	2.66494	76.23
36.211(6)	95(9)	0.19(2)	2.47870	89.22
41.49(2)	29(6)	0.24(5)	2.17477	27.45
50.23(1)	47(9)	0.18(5)	1.81479	44.10
54.865(7)	107(10)	0.20(3)	1.67201	100.00
58.41(9)	8(10)	0.2(2)	1.57867	7.64
63.45(3)	31(11)	0.3(1)	1.46488	28.71
65.11(2)	40(7)	0.22(6)	1.43156	36.95
72.97(3)	14(2)	0.17(5)	1.29546	13.33
76.81(3)	15(4)	0.21(6)	1.24001	13.95

Figure 1. XRD Pattern of Pure Cr₂O₃

Table 2. Peak list with their relative intensity of XRD of 1% Al doped Cr₂O₃

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
23.5116	58.06	0.1476	3.78391	99.56
32.5448	58.12	0.1476	2.75134	99.66
35.1311	55.45	0.1476	2.55449	95.08
40.4649	17.73	0.2952	2.22924	30.40
49.2204	21.94	0.2952	1.85124	37.62
53.8588	58.31	0.1968	1.70225	100.00
62.5259	24.08	0.2952	1.48552	41.30
64.1325	28.97	0.3936	1.45213	49.69
72.0428	9.97	0.7872	1.31092	17.10

Figure 2. XRD Pattern of 1% Al doped Cr₂O₃

Table 3. Peak list with their relative intensity of XRD of 2% Al doped Cr₂O₃

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
33.6057	35.11	0.3291	2.66687	85.21
36.1734	41.20	0.1686	2.48324	100.00
54.9401	24.43	0.3600	1.66990	59.29

Figure 3. XRD Pattern of 2% Al doped Cr₂O₃

Table 4. Peak list with their relative intensity of XRD of 3% Al doped Cr₂O₃

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
23.5072	108.23	0.1968	3.78461	75.72
32.5769	137.04	0.2460	2.74870	95.87
35.2087	142.94	0.1968	2.54904	100.00
40.5507	50.78	0.1968	2.22472	35.53
49.2748	65.32	0.1476	1.84933	45.70
53.8789	122.59	0.2460	1.70167	85.77
62.5157	43.75	0.1968	1.48574	30.60
64.1697	67.36	0.2952	1.45138	47.13
72.1453	16.57	0.5904	1.30931	11.59
75.8994	9.25	1.1808	1.25362	6.47
78.2299	9.17	0.3936	1.22201	6.41

Figure 4. XRD Pattern of 3% Al doped Cr_2O_3

Table 5. Peak list with their relative intensity of XRD of 5% Al doped Cr_2O_3

Pos. [$^{\circ}2\text{Th.}$]	Height [cts]	FWHM Left [$^{\circ}2\text{Th.}$]	d-spacing [$\text{\AA}$]	Rel. Int. [%]
23.4458	91.35	0.1968	3.79438	59.27
32.5640	141.82	0.1968	2.74976	92.02
35.1958	154.12	0.1968	2.54995	100.00
40.4691	43.30	0.1476	2.22902	28.09
49.2920	44.28	0.2952	1.84872	28.73
53.8699	115.22	0.1968	1.70193	74.76
62.5360	31.98	0.3936	1.48531	20.75
64.2682	48.67	0.3444	1.44939	31.58
72.3135	7.92	1.1808	1.30668	5.14
76.1916	7.08	1.1808	1.24954	4.60

Figure 5. XRD Pattern of 5% Al doped Cr_2O_3

The calculated crystalline average size of Al doped Cr_2O_3 nanoparticles values are tabulated in Table 6.

Table 6. Variation in crystallite size with Al concentration

S.No	Concentration of Al	Crystallite average size from Scherrer formula
1	0%	14.56
2	1%	13.91
3	2%	12.86
4	3%	12.16
5	5%	10.86

From Table 6, the average size of pure Cr_2O_3 is observed as 14.56 nm which decreases to 10.86 nm as the concentration of Al increases from 1% to 5%. This decrease in average size of nanoparticles with increase of Al concentration due to the increase in the densities of nucleation centers and thus to grow resulting in small crystallites

SEM and EDAX Studies

Scanning Electron Microscopy and Energy dispersive

X-ray analysis (EDAX) studies were carried out. Scanning Electron micrographs were obtained using a VEGA3 TESCAN Instrument. Energy dispersive X-ray analysis (EDAX) was used to estimate the composition of the materials using a Bruker CAL 4231 Model attached with Energy Dispersive Spectrometer of EDAX inc. USA.

SEM images of pure Cr_2O_3 and 1%, 2%, 3%, 5% Al doped Cr_2O_3 are shown in figures 6-10. These micrographs exhibited the formation of nanoparticles of Cr_2O_3 and Al doped Cr_2O_3 . From the images it can be considered the particles of Al doped are smaller in size as compared to pure Cr_2O_3 and the images are well distinguishable also verifies the difference in from Scherrer formula's result in Table 6. To check the chemical composition of the material, an energy dispersive X-ray (EDS) spectroscopy analysis was performed. Figure 11 shows the EDS spectra of 2% Al doped Cr_2O_3 nanoparticles which confirm the synthesis of Al doped Cr_2O_3 nanoparticles. The surface of the Cr_2O_3 and Al doped nanoparticles also exhibited elements of O, Cr and Al. Here the aluminium is present in elemental form. These results are consistent with the XRD data.

Figure 6. SEM image of Pure Cr_2O_3

Figure 7. SEM image of 1% Al doped Cr_2O_3

Figure 8. SEM image of 2% Al doped Cr_2O_3

Figure 9. SEM image of 5% Al doped Cr_2O_3
Figure 10. SEM image of 5% Al doped Cr_2O_3

Figure 11. EDAX image of 2% Al doped Cr_2O_3

Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectra were recorded in Perkin Elmer 100 spectrophotometer based in Najran University Saudi Arabia. The composition and quality of the material was investigated by the FTIR spectroscopy. The FTIR spectra of pure Cr_2O_3 nanoparticles are shown in Figure 12. The spectra shows the Cr-O bond appear at around $450\text{--}490\text{ cm}^{-1}$. The band at around 490 cm^{-1} may be related with oxygen vacancy or oxygen deficiency in Cr_2O_3 . This oxygen deficiency should translate into an enhanced green emission in UV absorption spectra.

Figure 12. FTIR Spectrum of pure Cr_2O_3 nanoparticles

Figure 13. FTIR Spectrum of 1% Al doped Cr_2O_3 nanoparticles

Figure 14. FTIR Spectrum of 2% Al doped Cr_2O_3 nanoparticles

Figure 15. FTIR Spectrum of 3% Al doped Cr_2O_3 nanoparticles

Figure 16. FTIR Spectrum of 5% Al doped Cr_2O_3 nanoparticles

The peaks at 1350 cm^{-1} correspond to the C-O absorption of Cr_2O_3 surface. The weak absorption band at 2367 cm^{-1} stands for carbonate that probably comes from the atmospheric carbon dioxide during synthesis. The broad peaks around 3429 cm^{-1} is assigned to the O-H stretching mode of hydroxyl group and 1634 cm^{-1} (bending) are due to asymmetrical stretching of the chromium carboxylate. The FTIR spectra of 1% Al, 2%, 3%, 5% **aluminium doped Cr_2O_3 nanoparticles** in different concentration of Al are shown in Figures 13-16. In FTIR studies it is found that there are no significant changes as the concentration of Al increases.

UV-Visible Absorption Spectroscopy Studies

The spectrum of absorption versus wavelength was recorded in Shimadzu UV Spectrophotometer. The optical absorption spectra of pure Cr_2O_3 and 1%, 2%, 3% and 5% Al doped Cr_2O_3 as the function of wavelength ranging from 0 to 1500 nm are shown in figures 17-21.

Figure 17. UV-Vis Spectrum of pure Cr_2O_3 nanoparticles

For pure Cr_2O_3 nano particles, the absorption intensity decreases sharply and suddenly for wavelength at 248nm. This was assigned to the intrinsic band gap of the Cr_2O_3 due to electron transitions from the valence band to the conduction band. Then the absorption intensity decreases slowly as the wavelength increases. After being doped with Al, the absorption peaks shifted towards longer wavelength at 277 nm i.e. red shifted. With doping of aluminium, the absorption spectra shows broadness after the UV peak which might be caused by the surface related defects in the nano particles. The UV emission band is probably due to the radiative recombination of excitons in the surfaces of Cr_2O_3 particles and the visible emission band results from the transition associated with the deep levels due to the oxygen vacancy.

Figure 18. UV-Vis Spectrum of 1% Al doped Cr_2O_3 nanoparticles

Figure 19. UV-Vis Spectrum of 2% Al doped Cr_2O_3 nanoparticles

Figure 20. UV-Vis Spectrum of 3% Al doped Cr_2O_3 nanoparticles

Figure 21. UV-Vis Spectrum of 5% Al doped Cr_2O_3 nanoparticles

Band Gap Determination

The optical band gap of the nanopowders was determined by applying the Tauc relation as given below $\alpha h\nu = B(h\nu - E_g)^n$, where α is the absorption coefficient [AC] ($\alpha = 2.303A/t$, here A is the absorbance and t is the thickness of the cuvette), B is a constant, h is Planck's constant, ν is the photon frequency, and E_g is the optical band gap. The value of $n = 1/2, 3/2, 2$ or 3 depending on the nature of the electronic transition responsible for absorption and $n=1/2$ for direct band gap semiconductor. An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ on the Y-axis and photon energy ($h\nu$) on the X-axis (Tauc Plot) gives the value of the optical band gap (E_g) as shown in Figures 22-26. The band gap values found from the Tauc plots are shown in table 7 for all samples.

Table 7. Variation in optical band gap with Al concentration

S.No	Al Concentration	Optical band gap (eV)
1	0%	3.48
2	1%	2.12
3	2%	2.10
4	3%	1.95
5	5%	1.90

From the table 7, the optical band gap for the undoped Cr_2O_3 is observed as 3.48 eV. On doping with different concentrations from 1% to 5% of Al, E_g value decreases from 3.48eV to 2.12eV.

Figure 22. Plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for undoped Cr_2O_3 **Figure 23.** Plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for 1% Al doped Cr_2O_3 **Figure 24.** Plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for 2% Al doped Cr_2O_3 **Figure 25.** Plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for 3% Al doped Cr_2O_3 **Figure 26.** Plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for 5% Al doped Cr_2O_3

4. Conclusions

In this paper, we have described the synthesis, structural, morphological and optical characterization of a series of Al doped Cr_2O_3 nanoparticles by simple cost effective solvothermal microwave irradiation technique. Aluminium doped Cr_2O_3 nano particles were prepared by using chromium nitrate and triethanolamine as template and aluminium nitrate in different concentrations (1%, 2%, 3%, 5%) as the source for aluminium dopant. Regarding the structural properties, a systematic decrease in the unit cell volume, crystallite size, and changes in the FWHM parameter were observed in concurrence with the presence of Al dopant in the prepared nanoparticles. The best results were obtained. The structure and phase of the as prepared materials were determined by using the XRD. The average size of the particles was measured by Scherer formula for both doped and pure Cr_2O_3 . The morphology and structural analysis was done by the SEM. Further the presence of aluminium dopants was confirmed EDAX. And prepared nano particles were also analyzed for FTIR, UV-Visible spectroscopic techniques. The optical band values (Eg) values were further obtained from Tauc plots.

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