RESEARCH ARTICLE OPEN ACCESS

Structural and Morphological Properties of Cr_2O_3 Nanoparticles Synthesized By Novel Solvent Free Method

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Abstract
Nanoparticles of chromium oxide (Cr_2O_3) are widely used in many fields serving as catalysts, wear resistance materials, and advanced colorants. For the first time, we have reported the solvent free synthesis of Cr_2O_3 nanoparticles via microwave irradiation followed by calcinations at 200, 400, 600 and 800°C for 1h. The influence of calcination temperature on the particle size, microstructure and morphology was examined by X-ray diffraction, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM), Elemental compositions have been estimated by energy dispersive X-ray Absorption EDAX and thermo gravimetrv analysis (TGA-DTA). The average particle size of the synthesized Cr_2O_3 nanoparticles is calculated using the Scherrer's formula and found to be of less than 60 nm and is compared with Williamson Hall method . It is found that the molar ratio 1:3 is considered to be the best proportion to synthesis Cr_2O_3 nanoparticles. These results also indicate that there is an improvement in the crystallinity of Cr_2O_3 nanoparticles with the increase in the annealing temperature. As the process is simple and low-cost, it has the potential to be produced on a large scale.
Keywords*: Nanoparticles, chromium oxide, microwave irradiation, calcined.*

I. Introduction

In the emerging field of nano technology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species. Nanostructured materials, characterized by small grain size (100 nm or less) and large surface area often exhibit novel catalytic, optical, magnetic and electrical properties relative to those of the coarse-grained counterparts [1–3]. During the past decade, considerable progress in the synthesis of nanoparticles has been achieved. Nanomaterials, particularly transition metal oxides play an important role in many areas of chemistry, physics and material science. Metal oxides have wide band gap because of significant contribution of ionic character to the chemical bonds between the metallic cat ions and oxide ions. In general metal oxides are not electrically conducting. However, current interest in material science is in unraveling the fundamental aspects of transparent conducting oxides and their applications as semiconducting and conducting transparent thin films.

In particular, nanostructured chromium (III) oxide (Cr_2O_3) with high specific surface area has attracted considerable attention in recent years [4–8]. For nanoparticles of Cr_2O_3, can be widely used in fields such as catalyst [9,10] coating, wear and corrosion wear resistance [11-15], advanced colorant [16-18], H_2 absorption material[19,20] , humidity sensing [21] and so on, it is significant to find an economical process which can be used to prepare them on a large scale. Chromic oxide (Cr_2O_3) is an important refractory material due to its high melting temperature (about 2300°C) and oxidation resistance; although its sinter-ability is very poor and requires special sintering condition to achieve high density. For such an application, the availability of nano sized powders would be desirable since they usually present high surface areas and may favor the sintering process. In addition, this kind of powders is essential for preparing nano crystalline ceramics, which may present improved properties (hardness, toughness, etc.) over the conventional ones.

There have been some ways to obtain Cr_2O_3 nano particles, including microwave plasma, decomposition of chromium (III) nitrate solution, laser-induced deposition, sono chemical reaction, precipitation, mechano-chemical process gas condensation and so on. But since either these processes are complex or their reaction apparatus are expensive, most of them have difficulties in being industrialized. Some new methods of preparation should be explored to meet the demands of industrialization. The purpose of this work is to find a

simple way to synthesize nano particles of Cr_2O_3 and is obtained successfully via novel solvent free microwave irradiation technique by the reaction system of $CrCl_3.6H_2O$ and NH_2-CO-NH_2. Meanwhile, the effect of the molar ratio and the relationship between the structure of the crystals, time and temperatures of calcinations will be studied. The microstructures of Cr_2O_3 nano crystals are characterized by means of X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Elemental compositions have been estimated by energy dispersive X-ray Absorption EDAX and thermo gravimetrv analysis (TGA-DTA).

II. Experimental

2.1. Materials and procedure

Chromium chloride ($CrCl_3.6H_2O$, 99%) and Urea (NH_2-Co-NH_2, 99%) were purchased as a pure reagent from Sigma Aldrich, Missouri, USA and has been used as received without any further purification treatment. Chromium oxide nano-powder has been obtained via the reaction of $CrCl_3.6H_2O$ and urea using solvent free method. Urea was added at room temperature to $CrCl_3.6H_2O$ with different molar ratios 1:1, 1:2 and 1:3 respectively. The resulting mixture is mixed thoroughly using a rod attached with motor whose rotation speed is 4000 rpm for about 20 to 30 minutes. Then the mixture is placed under microwave irradiation for about 35 to 40 minutes operated with frequency 2.45 GHz and power 800 W. Change in colour of material to deep green indicates the completion of reaction. The fine powder collected as yield at the end of microwave irradiation, were then calcined at 200, 400, 600 and 800°C for 1h in order to improve the ordering of Cr_2O_3 nano particles. During the calcination process the green gel is converted to black grey color.

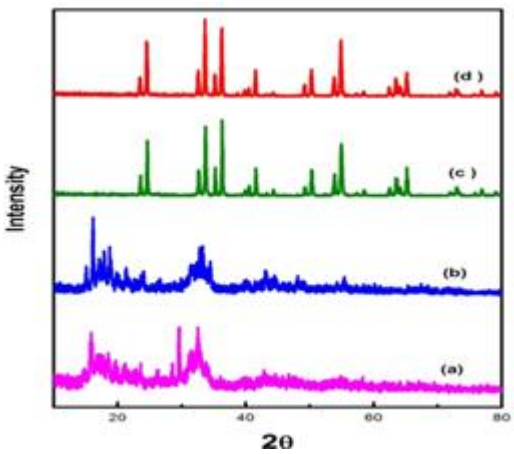


Fig 1. Powdered XRD pattern of the as prepared and the calcined Cr_2O_3 at 200, 400, 600 and 800°C .

2.2.1. X-ray diffraction and spectroscopic analyses

X-ray powder diffraction (XRD) was carried out on a (SEIFERT) PTS 3003 with CuKα radiation (λ=1.5406Å), operating at 40 kV and 10 mA. The diffraction data were recorded for 2θ values between 20° and 80° and the scanning rate was 10° min−1.

2.2.2. Scanning Electron Microscope (SEM) and Elemental energy dispersive X-ray Absorption (EDAX) analyses

Elemental compositions have been estimated by energy dispersive X-ray Absorption (EDAX). The morphology and structure were determined by scanning electron microscope (SEM). SEM was conducted on a JEOL 8900 electron microscope on Pt-coated samples.

2.2.3. *Thermal analyses*

Thermogravimetry (TG) and differential thermogravimetry (DTA) were performed by heating the sample at a rate of 10°C/min using a Shimadzu-50H analyzer (Japan) in N_2 atmosphere.

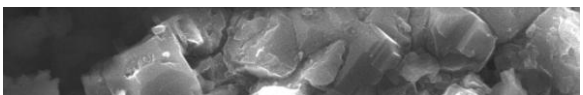
III. Results and Discussion

The calcined samples were characterized by powder XRD analysis on a (SEIFERT) PTS 3003 with CuKα radiation (λ=1.5406Å) to discuss the variation of structural morphology with calcined temperature. The results are discussed herein.

Sample	Particle size(nm)	a (Å)	c (Å)	V (CD)
As prepared	33.45	4.951	13.598	289.75
Calcined at 200°C	31.96	4.954	13.66	288.75
Calcined at 400°C	35.11	4.954	13.66	290.33
Calcined at 600°C	60.54	4.958	13.594	292.49
Calcined at 800°C	62.24	4.958	13.594	293.49

Table 1. Particle size & Lattice parameters at various calcination temperature

Fig. 1 depicts the XRD pattern of as prepared and calcined Cr_2O_3 nanoparticles at various temperatures. It can be seen that all diffraction peaks are well defined which indicates that Cr_2O_3 nanoparticles are perfectly crystallized. Based on the XRD pattern, the as prepared sample itself shows crystalinity. However to understand the Cr_2O_3 phase evolution, calcinations was performed at 200, 400, 600 and 800°C. Inspection of the results revealed that Cr_2O_3 thus formed is of rhombohedral phase (JCPDS no. 01-1294 with a=4.9504 Å, c=13.5686 Å and space group $R\bar{3}c$). The major peaks were indexed as



(1 0 4), (1 1 0),(2 0 2),(1 1 3),(0 2 4),(3 0 0), and (2 2 0). Table 2 depicts the coincidence of 2θ values as obtained by XRD pattern with that of standard JCPDS values.

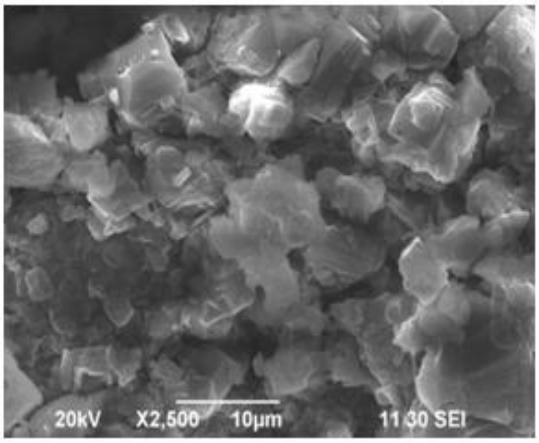


Fig 2. Sem image of Cr_2O_3

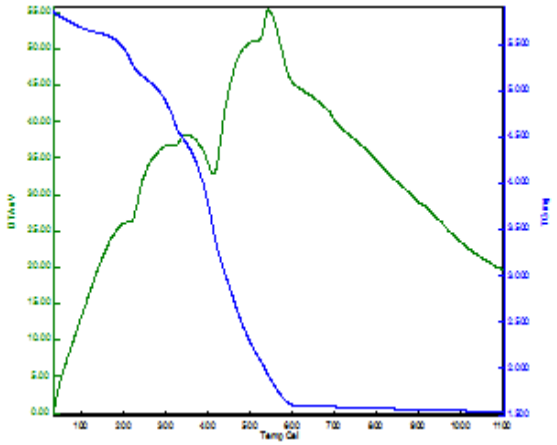


Fig 3. TGA-DTA of Cr_2O_3

It is obvious that there is an improvement in the crystallinity of Cr_2O_3 nanoparticles with the increase in the annealing temperature. Table.1 shows the effect of annealing temperature on the crystallite size. When the annealing temperature is increased to 200°C, the minimum crystallite size of 31.96 nm is obtained. Further increase in the annealing temperature results in the increase of the crystallite size.

Fig.2 shows the SEM photographs of the as-synthesized chromium oxide nanopowders. It can be observed that nanoparticles are nearly rhombohedral and isolated. It is also clear that the nano particles size decreased with calcination. The non-agglomerated Cr_2O_3 nano particles obtained in the present investigation are comparable to ones produced by using templates.

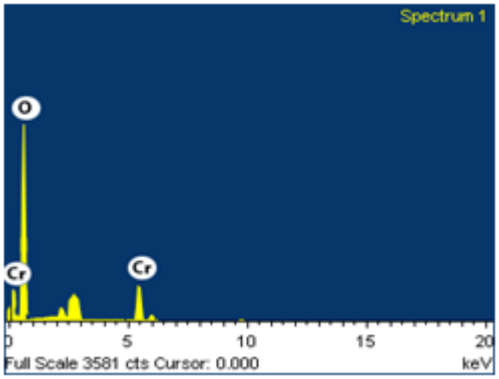


Fig 4. EDAX spectra of Cr_2O_3

To identify the decomposition temperature of chromium oxide, the thermo gravimetric analysis was conducted on the chromium oxide (Cr_2O_3) powder under flowing nitrogen. The differential thermal and thermo gravimetric curves obtained for the crystalline Cr_2O_3 nano particles are shown in Fig 3. As observed the main features of the DTA curve are an endothermic peak centered at 412°C followed by an exothermic peak centered at 543°C respectively. From TGA, it is clear that the decomposition of the sample started at about 230^0C with a weight loss of 10.8% which may correspond to the loss of half the molecule of oxygen. The endothermic effect, which is accompanied by a weight loss of 21.7% measured between 330°C, may correspond to the loss of one molecule of oxygen. Finally at 600°C,a weight loss of 72 % is observed which may correspond to the loss of two chromium atoms.

To investigate the atomic percentage and stoichiometry level of our samples, the chemical composition is checked by energy dispersive X-ray diffractograms and is shown in Fig.4.

IV. Conclusion

A new method of preparation should be explored to meet the demands of industrialization. In this research, n type transparent conducting oxide nano particles of Cr_2O_3 were obtained successfully via novel solvent free microwave irradiation technique by the reaction system of $CrCl_3.6H_2O$ and NH_2-CO-NH_2. The novel, cost effective and simple method discussed by us provides particle size of 20 – 58 nm. The structural properties were discussed briefly for choosing the appropriate composition and crystallite size as required for specific applications. The heating technique also influences the size and shows that there is an improvement in the crystallinity of Cr_2O_3 nanoparticles which leads to fine quantum confinement with the increase in annealing temperature. The SEM and TGA-DTA analysis of the samples are also performed.

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