Structural and Morphological Properties of Cr$_2$O$_3$ Nanoparticles Synthesized By Novel Solvent Free Method

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Abstract
Nanoparticles of chromium oxide (Cr$_2$O$_3$) 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$_2$O$_3$ 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 gravimetry analysis (TGA-DTA). The average particle size of the synthesized Cr$_2$O$_3$ 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$_2$O$_3$ nanoparticles. These results also indicate that there is an improvement in the crystallinity of Cr$_2$O$_3$ 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$_2$O$_3$) with high specific surface area has attracted considerable attention in recent years [4–8]. For nanoparticles of Cr$_2$O$_3$ 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. Chronic oxide (Cr$_2$O$_3$) 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$_2$O$_3$ nanoparticles, 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$_2$O$_3$ and is obtained successfully via novel solvent free microwave irradiation technique by the reaction system of CrCl$_3$,6H$_2$O 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$_2$O$_3$ 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 gravimetry analysis (TGA-DTA).

II. Experimental

2.1. Materials and procedure

Chromium chloride (CrCl$_3$,6H$_2$O, 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$_2$O and urea using solvent free method. Urea was added at room temperature to CrCl$_3$,6H$_2$O 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$_2$O$_3$ nano particles. During the calcination process the green gel is converted to black grey color.

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 ($\lambda=1.5406\text{Å}$), operating at 40 kV and 10 mA. The diffraction data were recorded for 20 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 ($\lambda=1.5406\text{Å}$) to discuss the variation of structural morphology with calcined temperature. The results are discussed herein.

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

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

Fig. 1. Powdered XRD pattern of the as prepared and the calcined Cr$_2$O$_3$ at 200, 400, 600 and 800°C.
(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 Cr₂O₃](image)

It is obvious that there is an improvement in the crystallinity of Cr₂O₃ 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 Cr₂O₃ nano particles obtained in the present investigation are comparable to ones produced by using templates.

![Fig 3. TGA-DTA of Cr₂O₃](image)

To identify the decomposition temperature of chromium oxide, the thermo gravimetric analysis was conducted on the chromium oxide (Cr₂O₃) powder under flowing nitrogen. The differential thermal and thermo gravimetric curves obtained for the crystalline Cr₂O₃ 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°C 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.

![Fig 4. EDAX spectra of Cr₂O₃](image)

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 Cr₂O₃ were obtained successfully via novel solvent free microwave irradiation technique by the reaction system of CrCl₃.6H₂O and NH₂-CO-NH₂. 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 Cr₂O₃ 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.
References