Optical, Structural, Morphological Properties of Chromium (III) Oxide Nanostructure Synthesized Using Spray Pyrolysis Technique

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Abstract
Nanostructure of chromium oxide (Cr$_2$O$_3$-NPs) with rhombohedral structure were successfully prepared by spray pyrolysis technique using Aqueous solution of Chromium (III) chloride CrCl$_3$ as solution. The films were deposited on glass substrates heated to 450 °C using X-ray diffraction (XRD) shows the nature of polycrystalline samples. The calculated lattice constant value for the grown Cr$_2$O$_3$ nanostructures is a = b = 4.959 Å & c = 13.594 Å and the average crystallize size (46.3-55.6) nm calculated from diffraction peaks, Spectral analysis revealed FTIR peak characteristic vibrations of Cr-O Extended and Two sharp peaks present at 630 and 578 cm$^{-1}$ attributed to Cr-O “stretching modes”, are clear evidence of the presence of crystalline Cr$_2$O$_3$. The energy band gap (3.4 eV) for the chromium oxide nanostructures was measured using the UV-VIS-NIR Optical Spectrophotometer. It was found that by scanning electron microscopy (SEM) and image results, there is a large amount of nanostructure with an average crystal size of 46.3-55.6 nm, which indicates that our synthesis process is a successful method for preparing Cr$_2$O$_3$ nanoparticles.

1. Introduction
The study of microstructure and nanostructure has received increasing attention because of the new properties that materials may exhibit when reducing grain size [1]. Over the past decades, much progress has been made in the manufacture of nanostructure. "Nanomaterials", especially Transitional metal oxides have an important role in materials science, physics and chemistry as well as technological applications [2]. Metal oxides are commonly used in the manufacture of sensors, electronic circuits, fuel cells, and Coatings for corrosion-resistant surfaces and as a catalyst [3]. Nanostructure of metal oxides can have unique chemical properties due to their specific size and high density of edge surface locations [3,4]. Among the inorganic nanostructure, chromium nanostructure (III) (Cr$_2$O$_3$) has got a lot of attention due to their wide applied fields, including pigment [5], "heterogeneous catalysts" [6,7]. Coating materials for the purpose of thermal protection [8,9], biological applications [10,11], digital recording system [12], photonic and electron ic devices [13,14]. Various techniques were developed for the assembly of Cr$_2$O$_3$ nanostructure such as hydrothermal [15], Solid pyrolysis [16], combustion [17], sol-gel [18], precipitation gelation [19], oxidation chromium [20], laser-induced deposition [21], mechanochemical reaction and subsequent heat Treatment [22], and "sonochemical methods" [23]. Many preparation methods, such as: sol-gel technology, "laser induced deposition", "hydrothermal reduction", chemical-mechanical reaction, "condensation–polymerization", "gas condensation", solid pyrolysis, homogeneous precipitation with the help of urea, microwave plasma,"sono-chemical reaction", thermal...
treatments, nano-casting method, hydrazine reduction and solution-combustion synthesis were used to prepare Cr$_2$O$_3$ nanostructures [24]. Most of these techniques are cost-effective, complex, require high temperature, environmentally sensitive and special laboratory equipment. Therefore, for the current study, a typical hydrothermal method was used to synthesize Cr$_2$O$_3$ nanostructures due to the fact that this preparation method reduces cost and is straightforward at low temperature.

In this paper a simple and important method for the synthesis of nanosized Cr$_2$O$_3$ chromium oxide by spray pyrolysis technique in nano is described. The surface properties, size, morphology and crystallographic structure of Cr$_2$O$_3$ particles are characterized by means of X-ray diffraction (XRD), and scanning electron microscope (SEM) which will give much valuable information about these materials. In addition, optical properties of chromium (III) oxide (Cr$_2$O$_3$) nanostructure which determined using the UV-VIS-NIR Optical Spectrophotometer.

2. Experimental work

An aqueous solution of Chromium (III) chloride CrCl$_3$ (Sigma-Aldrich Labor) was prepared by dissolving 0.15M of “chromium chloride” in 100 ml in “distilled water” with constant moving for 45 minutes. In order to keep the pH value of the solution at 10, we added a few drops of “ammonium hydroxide” to the solution while moving. Chromium (III) chloride react with water to produce hydrogen chloride and chromium (III) oxide using compressed air as a carrier gas [25].

$$2\text{CrCl}_3 + 3\text{H}_2\text{O} \ [\text{temp}] = 6 \text{HCl} + \text{Cr}_2\text{O}_3$$

The precursor solution was transformed into an aerosol by an ultrasonic nebulizer operating at a frequency of 1.7 MHz, which is connected to the precipitation chamber via a spray nozzle where the precipitation process takes place inside the chamber on a glass substrate at a temperature of (450 ± 5) °C, it has been maintained, the nozzle-substrate distance at 7cm where the spraying continues for five minutes.

In this part of the experiment, thin films of chromium oxide were prepared use the aerosol generated in the ultrasonic nebulizer was injected into the stainless-steel chamber through a nozzle as shown in Fig.1 with deposition time (5 min) to get required layer of Cr$_2$O$_3$ thin film. The film prepared from Cr$_2$O$_3$ was green in color and had good adhesion to glass substrates as it was tested by visual inspection.

![Figure 1: Schematic diagram for system set up.](image-url)
3. Results and discussion

3.1. X-Ray and FTIR studies

The X-ray diffraction was carried out on "a Philips Analytical XPERT". Using a diffractometer "Cu Kα radiation (λ = 1.54056Å) with a "MINIPROP detector", it works at 40 Kv and 30 mA. It was recorded X-ray diffraction patterns between 2θ =10° to 80°. shows the XRD pattern (Fig. 2), it can be observed peaks that belong to the crystalline phases of Cr$_2$O$_3$ (012), (104), (110), (113), (024), (116) and (300). All peaks can be set to Cr$_2$O$_3$ stage according to data released by the "ICDD (International Center for Diffraction Data) cards", No. card (00-038-1479). The average crystallite sizes were calculated using the Scherrer equation D=Kλ/(βcosθ) where, λ = 1.54056 Å is the wavelength of an X-ray, K = 0.9 is the “Scherer constant” β is (FWHM) and “θ” is the “Bragg diffraction angle”. The calculated lattice constant value for the grown Cr$_2$O$_3$ nanostructures is a = b = 4.959 Å & c = 13.594 Å whereas reported [26]value for lattice constant is a=b=4.953 Å & c=13.578 Å. The recorded and calculated values of the lattice constants agree well. Table (1) shows the size of the grains for the prepared sample, which is agreed with the report [27].

![Figure 2: XRD model of Cr$_2$O$_3$ nanostructure prepared by spray pyrolysis.](image)

Table 1: Experimental and standard values of peaks, and grain size of Cr$_2$O$_3$ sample prepared with SP technique.

| 2θ (deg) | dhkl (Exp.) (Å) | dhkl (Std.) (Å) | hkl | FWHM (deg) | G.S (nm) |
|----------|-----------------|-----------------|-----|------------|----------|
| 24.5055  | 3.62965         | 3.63132         | 012 | 0.167      | 46.354   |
| 33.5954  | 2.6656          | 2.66533         | 104 | 0.1651     | 47.958   |
| 36.1976  | 2.47959         | 2.4796          | 110 | 0.1575     | 51.524   |
| 41.4719  | 2.17561         | 2.1752          | 113 | 0.6950     | 50.4     |
| 50.2167  | 1.81533         | 1.81521         | 024 | 0.1609     | 49.677   |
| 55.2476  | 1.66133         | 1.67237         | 116 | 0.1433     | 55.662   |
| 65.0980  | 1.43173         | 1.43157         | 300 | 0.1738     | 46.354   |

Figure 3 shows the "Fourier-transform infrared" (FTIR) spectra of chromium oxide (Cr$_2$O$_3$) sample prepared by SP technique. As it can be observed, at a frequency of 3420 cm$^{-1}$, where the broad band, it is compatible with the "stretching modes" of OH groups. Generally, Cr$_2$O$_3$ absorption bands appear below 1000 cm$^{-1}$ due to "inter-atomic vibrations". Two sharp peaks present at 630 and 578 cm$^{-1}$ attributed to Cr-O "stretching modes", are clear evidence of the presence of crystalline Cr$_2$O$_3$ [28].
3.2. Morphological analysis

The morphology of Cr$_2$O$_3$ nanostructure prepared with SEM images was distinguished as shown in Fig. 4. From the images results, it can be noticed that a large amount of nanostructure (NPs) with an average crystallite size of 46.3-55.6 nm, which indicates that our synthesis process is a successful method to prepare Cr$_2$O$_3$ nanoparticle.

3.3. Optical analysis

Figure 5 shows the “optical absorption spectrum” of the Synthesized Cr$_2$O$_3$ nanostructure. The spectrum shows the generic direction of absorption, i.e., reduced absorption of material with a decrease in the frequency of incident radiation. Figure 6, shows the alteration of $(h\nu \alpha)^2$ with photon energy (h$\nu$) for the synthesized Cr$_2$O$_3$ thin film of thickness 170 nm, the film thickness was measured by a thin film measuring system (Stellar Net Inc. Thin Film measurement systems), which works on the principle of spectroscopy. The plot shows the direct band gap of $\sim$3.4 eV, which is agreed with the report [29].
4. Conclusions

Using spray pyrolysis technology, a thin film of chromium oxide nanostructure was fabricated using simple chromium chloride materials as primers. The results were obtained by XRD, FTIR, SEM, and UV-VIS spectrometers. Identical and specific crystal phase (Cr$_2$O$_3$), bonding (Cr-O), purity (Cr, O) and energy bandgap (3.4 eV) of Cr$_2$O$_3$ nanostructures. The average crystallizes size (46.3-55.6) nm calculated from diffraction peaks indicating the formation of a nanostructured layer.

Acknowledgements

We would like to show our gratitude to department of physics (laser and molecular group) in Baghdad university to allow us to use their lab to accomplish this work.

Conflict of interest

We certify that we have NO affiliations with or involvement in any organization or entity with any financial interest.
References
1. Khan I., Saeed Kh., *Nanoparticlees: properties, applications and toxicities*. Arabian Journal of chemistry, 2019. 12(7): pp. 908-931.
2. Gesheva K., Ivanova T., Bodurov G., Szilagyi I. M., Justh N., *Technologies for deposition of transition metal oxide thin films: application as functional layers in “smart windows” and photocatalytic systems*. Journal of physics 2016. conference series 682.
3. Fernandez-Garcia M., Martinez-Arias A., Hanson J. C. and J. A. Rodriguez, *Nanostructured Oxides in Chemistry Characterization and properties*, Chemical Reviews, 2004. 104(9): pp. 4063-4104.
4. Oun A. A., Shankar Sh. and Rhim J., *Multifunctional nanocellulose/metal and metal oxide nanoparticle hybrid nanomaterials*. Critical Reviews in Food Science and Nutrition 2019. 60(3), 435-460.
5. Hebbar D., Choudhari K. S., Shivashankar S. A., Santhosh C., Kulkarni S. D., *Facile microwave-assisted synthesis of Cr$_2$O$_3$ nanostructure with high near-infrared reflection for roof-top cooling applications*. Journal of Alloys and compounds, 2019. 785: pp. 747-753.
6. Karimiana R., Prib F., *Synthesis and Investigation the Catalytic Behavior of Cr$_2$O$_3$ Nanoparticles*. JNS, 2013. 3: pp. 87-92.
7. Wang G., Zhang L., Deng J., Dai H., He H., Au Ch. Tong, *Preparation, characterization, and catalytic activity of chromia supported on SBA-15 for the oxidative dehydrogenation of isobutene*. Applied Catalysis A: General, 2009. 355(1-2); pp. 192-201.
8. Chang T., Cao X., Li N., Long S., Gao X., Dedon L. R., Sun G., Luo H. and Jin P., *Facile and Low-Temperature Fabrication of Thermochromic Cr$_2$O$_3$/VO$_2$ Smart Coatings: Enhanced Solar Modulation Ability, High Luminous Transmittance and UV-Shielding Function*. ACS Appl. Mater. Interfaces. 2017. 9(31): pp. 26029-26037.
9. Singh Sh. P., Chinde S., Kamal S. S., Rahman M. F., Mahboob M., Grover P., *Genotoxic effects of chromium oxide nanoparticles and microparticles in Wistar rats after 28 days of repeated oral exposure*. ESPR, 2015. 23: pp. 3914–3924.
10. Hassan D., Talhakhilil A., Solangi A. R., El-Mallul A., Shinwari Z. Kh., Maaza M., *Physicochemical properties and novel biological applications of Callistemon viminalis-mediated α-Cr$_2$O$_3$ nanoparticles*. Applied Organometallic Chemistry, 2019. 33(8).
11. Lu M., Cui Y., Zhao S., Fakhri A., *Cr$_2$O$_3$/cellulose hybrid nanocomposites with unique properties: Facile synthesis, photocatalytic, bactericidal and antioxidant application*. Journal of Photochemistry and Photobiology B: Biology, 2020. 205.
12. Bijker M. D., Bastiaens J. J. J., Draaisma E. A., de Jong L. A. M., Sourty E., Saied S. O. Sullivan J. L., *The development of a thin Cr$_2$O$_3$ wear protective coating for the advanced digital recording system*. Tribology International, 2003. 36(4-6); pp. 227-233.
13. He X., Antonelli D., *Synthesen und Anwendungen von übergangsmetalhaltigen mesoporösen Molekularsieben*. Angew. Chem. Int. Ed, 2002.114(2): pp. 222-238.
14. He X., Antonelli D., *Recent Advances in Synthesis and Applications of Transition Metal Containing Mesoporous Molecular Sieves*. Angew Chem. Int. Ed, 2002. 41(2); pp. 214-229.
15. Hebbar D., Choudhari K. S., Shivashankar S. A., Santhosh C., Kulkarni S. D., *Facile microwave-assisted synthesis of Cr$_2$O$_3$ nanoparticles with high near-infrared reflection for roof-top cooling applications*. Journal of Alloys and compounds, 2019. 785: pp. 747-753.
16. Mohanapandian K. and Krishnan A., *Synthesis, Structural, Morphological and Optical Properties of Cu²⁺ Doped Cr₂O₃ Nanoparticles*. International Journal of Advanced Engineering Technology, 2016. **VIII**(II): pp. 273-279.

17. Wang H., Han W., Li X., Liu B., Tang H., Li Y., *Solution Combustion Synthesis of Cr₂O₃ Nanoparticles and the Catalytic Performance for Dehydrofluorination of 1,1,1,3,3-Pentafluoropropane to 1,3,3,3-Tetrafluoropropene Molecules*, 2019. **24**(2): pp. 361.

18. Sangwan P., Kumar H., *Synthesis, Characterization and Antibacterial Activities of Chromium Oxide Nanoparticles Against Klebsiella Pneumoniae*. Asian Journal of Pharmaceutical and Clinical Research, 2017. **10**(2): pp. 206-209.

19. Abdullah H. I. & Abbas L. J., *Photosynthesis of Chromium Oxide Nanoparticles from Chromium Complexes*. Ijapcr, 2017. **7**(1): pp. 1-8.

20. Tian S., Ye X., Dong Y., Li W., Zhang B., Li B., Feng H., *Production and Characterization of Chromium Oxide (Cr₂O₃) via a Facile Combination of Electrooxidation and Calcination*. International Journal of Electrochemical Science, 2019. **14**: pp. 8805-8818.

21. Karimian R., Piri F., *Synthesis and Investigation the Catalytic Behavior of Cr₂O₃ Nanoparticles*. JNS, 2013. 3: pp. 87-92.

22. Tsuzuki T., Mc Cormick P. G., *Synthesis of Cr₂O₃ Nanoparticles by mechanochemical processing*. Acta Materialia. 2000. **48**(11): pp. 2795-2801.

23. Alrehaily L. M., Joseph J. M. and Wren J. C., *Radiation-Induced Formation of Chromium Oxide Nanoparticles: Role of Radical Scavengers on the Redox Kinetics and Particle Size*. J. Phys. Chem. C 2015. **119**(28): pp. 16321-16330.

24. Abdullah M. M., Rajab Fahd M. and Al-Abbas Saleh M., *Structural and optical characterization of Cr₂O₃ nanostructures: Evaluation of its dielectric properties*. AIP Advances, 2014. **4**, 027121.

25. Rer, *characterization of Cr₂O₃ catalysts for Cl/F exchange reaction*. M.Sc. thesis, chemical Engineer, 2004. Humboldt University.

26. Al-sharuee I.F. and Mohammed F.H. *Investigation study the ability of superhydrophobic silica to adsorb the Iraqi crude oil leaked in water*. IOP Conference Series: Materials Science and Engineering, 2019. **571**(1): pp. 1-6.

27. Jamal A., Raahman M. M., Khan Sh. B., Abdullah M. M., Faisaal M., Asiri A. M., Aslam A., Khan P. and Akhtar K., *Simple Growth and Characterization of a-Sb₂O₃: Evaluation of their Photo-catalytic and Chemical Sensing Applications*. J. Chem. Soc. Pak. 2013. **35**(3): pp. 570-576.

28. Sone B. T., Manikandan E., Gurib-Fakim A. and Maaza M., *Single-phase α-Cr₂O₃ nanostructure green synthesis using Callistemon viminalis’ red flower extrac*, Green Chemistry Letters and Reviews, 2016. **9**(2): pp. 85–90.

29. Julkarmain M., Hossain J., Sharif K. S. and Khan K. A., *Optical properties of thermally evaporated Cr₂O₃ thin films*. Canadian Journal on Chemical Engineering & Technology, 2012. **3**(4): pp. 81–85.
الخصائص البصرية والمورفولوجية والهيكلية للبنية النانوية لواكسيد الكرم المصنعة باستخدام تقنية الانحلال الحراري

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الخلاصة

تم تحضير الهيكل النانوي لأكسيد الكرم (Cr$_2$O$_3$-NPs) ذات البنية المعينة بواسطة تقنية الانحلال الحراري بالرش باستخدام محلول مائي من كلوريد الكرم (CrCl$_3$) الذي يتم تخليطه باستخدام سائل مائي (XRD) الذي يظهر ان النماذج المرشدة ذات طبيعة متعددة التبلور قيمة ثابت الشبكة المحسوبة للبنى النانوية المزروعة هي a = b = 4.959 Å & c = 13.594 Å ومتوسط حجم التبلور كان بحدود (46.3-55.6) نانومتر. كما أن التحليل الطيفي لمقياس احترامات الاير (FTIR) كشف الاهتزازات المميزة لذروة Cr-O عند 630 و 578 سم^{-1} تُعزى إلى "أوضاع التمدد" Cr-O و Cr-O، وهي سائدة على وجود Cr$_2$O$_3$. تم قياس فجوة نطاق الطاقة (4.3 الكترون فولت) لليونات النانوية لأكسيد الكرم باستخدام مقياس الطيف الضوئي UV-Vis-NIR. لقد وجد أنه عن طريق مسح المجهر الإلكتروني (SEM) ومقياس الطيف الضوئي، هناك كمية كبيرة من البنية النانوية Cr$_2$O$_3$. بمتوسط حجم بلوري يبلغ 46.5-5.5 نانومتر، مما يشير إلى أن عملية التوليف لدينا هي طريقة ناجحة لإعداد الجسيمات النانوية Cr$_2$O$_3$. 