Chromium (III) Oxide Nanostructures Synthesized from Vernonia Amygdalina Leaves Extract

Asratemedhin B. Habtemariam 1,*, Ashenafi K. Kereta 1

1 Physics Department, College of Natural and Computational Sciences, Debre Berhan University, P. O. Box 445, Ethiopia
* Correspondence: asratemedhinbekele@dbu.edu.et; Scopus Author ID 7212268225
Received: 25.08.2020; Revised: 25.09.2020; Accepted: 28.09.2020; Published: 2.10.2020

Abstract: This contribution reports first time synthesis of Cr₂O₃ nanostructures from chromium (III) chloride hexahydrate precursor using Vernonia amygdalina leaves extract as a reducing and stabilizing agent. Powder X-ray diffraction, Fourier-transform infrared spectroscopy, and scanning electron microscopy techniques were used to study the structural and morphological properties of the as-synthesized Cr₂O₃ nanostructures. Powder X-ray diffraction patterns spectral analysis showed that hexagonal Cr₂O₃ nanostructures with an average crystallite size of 23.4 nm were synthesized with the minor appearance of CrO₂. SEM images showed that the synthesized nanomaterials are granules. Fourier-transform infrared spectra represent a sharp absorption band at 552 cm⁻¹, which indicates Cr-O-Cr vibrational and stretching modes.

Keywords: Bio-mediated; Cr₂O₃ nanostructures; granules; Vernonia amygdalina.
© 2020 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

Chromium (III) oxide (Cr₂O₃), among the various oxides of chromium, is the most stable oxide found in a wide range of temperature and pressure [1,2]. Cr₂O₃ is technologically important due to its numerous applications, including green pigment, catalysts, coating materials for UV protection, and visible light transmittance [3,4]. Cr₂O₃ is the hardest oxide that also exhibits many attractive functionalities among these lower coefficient of friction, high wear, and corrosion resistance, and good optical and adiabatic characteristics are key properties [5,6]. It also exhibits a high melting point (2435 ºC) and high-temperature oxidation resistance [7-9]. Despite its intrinsic insulator nature, Cr₂O₃ films can exhibit either p-type or n-type semiconductor behavior, depending on the synthesis conditions [1]. The confluence of all these properties in Cr₂O₃ makes it a preferable material for the development of a broad range of industrial applications.

Chromium (III) oxides can be synthesized by different methods such as thermal decomposition [9-11] precipitation [12], chemical vapour deposition [2], sol-gel [8], hydrothermal [13,14], solution combustion [15,16] and biological [1,17]. Among these, the biological (bio-mediated) method is non-toxic, inexpensive, and environmental friendly, which involves the use of bacteria, fungi, or plant materials to synthesize chromium (III) oxide, playing a significant role in controlling surface morphology and size of the material [18,19].

So far, fewer studies have been reported on the synthesis of Cr₂O₃ nanostructures using different plant extracts. For instance, nano-sized Cr₂O₃ nanoparticles were synthesized from potassium dichromate solution reduction using Tridax procumbens leaf extract, which acts as
a reducing agent [17]. Single-phase α-Cr₂O₃ nanoparticles’ were also synthesized using the red flower of Callistemon viminalis’ extract [1]. In the present study, Cr₂O₃ nanostructures were successfully synthesized using Vernonia amygdalina (V. amygdalina) plant leaves extract as a reducing and stabilizing agent.

V. amygdalina is a small evergreen tree (about five-meter tall), a very popular plant that grows, preferably in most parts of tropical Africa [20-22]. The plant is commonly called bitter leaf due to its bitter taste [21] and known as ‘Grawa’ in Amharic (Ethiopia). V. amygdalina is known for its high production, as its seeds propagate easily by wind, high adaptability, and its ability to improve the soil fertility and growth of crops [23]. In developing countries, disease treatment using herbal plants plays a key role in medication. In the rural highlands of Ethiopia, the water extract of V. amygdalina leaves serves as a traditional medicine for the prevention of stomach-ache as it is a non-toxic plant. Phytochemical analysis of V. amygdalina revealed high levels of flavonoids, phenol, saponin, tannins, and alkaloids [24]. It exhibits excellent antioxidant properties due to the presence of flavonoid and phenolic constituents [22,24], and this has been reported in an attempt to synthesize NiO nanoparticles [25].

2. Materials and Methods

2.1. Materials.

Chromium (III) chloride (Cr₂Cl₃•6H₂O) and distilled water were purchased from Sigma-Aldrich. Fresh and healthy leaves of V. amygdalina were collected from Hawariat town, Gurge zone in the South region, Ethiopia.

2.2. Synthesis of Cr₂O₃ nanoparticles.

Freshly collected and taxonomically authenticated leaves of V. amygdalina were washed thoroughly with tap water followed by distilled water to avoid dust and impurities and shade dried for a couple of weeks. The dried V. amygdalina leaves were powdered and stored in an airtight plastic bag for subsequent use.

To prepare the extract solution, a weighed 10 gm of the dried leaves were added into 100 ml of distilled water in a flask and boiled at 60 °C for 30 min. Then the extract was cooled to room temperature and filtered (Whatman No. 1) to get the brown color aqueous extract solution shown in Figure 1a, and a 0.1M solution of the precursor was prepared using CrCl₃•6H₂O as shown in Figure 1b.

The synthesis protocol employed was the commonly applied process [25]. In a typical experiment, 50 ml of the prepared precursor solution was mixed with 40 ml of V. amygdalina leaves extract solution in a beaker dropwise. After 30 min. The solution changes color from dark to green, indicating the formation of chromium oxide nanostructures (Figure 1c). The purpose of the plant extract here is to reduce and stabilize the synthesized nanostructures.
[26,27]. The solution was heated at 60 °C for 30 min. under continuous magnetic stirring. After cooling down to room temperature, the resulting solution was centrifuged at 3500 rpm and washed repeatedly using distilled water to avoid impurities. As it is assumed that Cr₂O₃ nanostructures can be obtained in the range of 110-217 °C [10], the final precipitate was oven-dried at a temperature of 120 °C. The dried powder was annealed at 500 °C in an air furnace for 2 hrs [1,15] to get Cr₂O₃ nanostructures.

3. Results and Discussion

3.1. X-ray diffraction (XRD) analysis.

For phase identification, X-ray diffraction (XRD) patterns were recorded from an X-ray diffractometer with 2 theta geometry, operating with CuKα radiation (λ=1.540598 Å) at a voltage of 40 kV and current of 30 mA. The XRD patterns of the powder sample were recorded with a step size of 0.02 at a scan speed of 3°/min and a counting time of 0.4 sec./step in the 10° to 80° 2θ range. The resulting XRD patterns of the as-prepared nanopowder can be indexed to the hexagonal structure of Cr₂O₃ from JCPDS card no. 96-210-4123 (Figure 2a), and the patterns are compared to the standard using match software Figure 2b). The peaks are indexed to 24.37°, 33.56°, 36.28º, 41.53º, 50.23º, 55.5º, 63.47º, and 65.47º, which corresponds to the crystal plane (102), (104), (110), (113), (204), (116), (214) and (300), respectively, of crystalline Cr₂O₃.

![Figure 2](https://nanobioletters.com/)

**Figure 2.** XRD patterns of Cr₂O₃ nanostructures(a) and Retvield refined XRD data (b).

Inter planar spacing ′d′ for hexagonal phase structure of Cr₂O₃, is determined by the following relation:

\[
\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2},
\]

where ‘h’, ‘k’, and ‘l’ are miller indices.

Average crystallite size \(D_{hkl}\) was estimated using the Scherrer equation from prominent XRD peaks:

\[
D_{hkl} = \frac{k \lambda}{\beta \cos \theta}
\]

where ‘k’ is a shape factor (k = 0.9), ‘\(\lambda\)’ is the X-ray wavelength, and ‘\(\beta\)’ and ‘\(\theta\)’ are the half-width of the peak and half of the Bragg angle, respectively. Using this equation, the crystallite sizes of Cr₂O₃ nanostructures was calculated to be 23.4 nm.
3.2. Fourier-transform infrared (FTIR) spectroscopy.

Spectral analysis was recorded using a Fourier-transform infrared instrument whose spectral range is from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). Figure 3a is representative FTIR spectra peak of *V. amygdalina* leaves extract indexed to 3354 cm\(^{-1}\), 2927 cm\(^{-1}\), 2857 cm\(^{-1}\), 1647 cm\(^{-1}\), 1402 cm\(^{-1}\), 1251 cm\(^{-1}\), 1059 cm\(^{-1}\) and 611 cm\(^{-1}\). The broad absorption band around 3354 cm\(^{-1}\) is related to the O–H bond stretching of the phenolic group, the peaks at 2927 cm\(^{-1}\) and 2857 cm\(^{-1}\) are related to the C–H bending, and the peaks at 1647 cm\(^{-1}\), 1402 cm\(^{-1}\), and 1251 cm\(^{-1}\) are related to the N–H bending [28]. The absorption spectra of Cr\(_2\)O\(_3\) nanostructures are observed at 3396 cm\(^{-1}\), 2920 cm\(^{-1}\), 2853 cm\(^{-1}\), 1605 cm\(^{-1}\), 1402 cm\(^{-1}\), 1039 cm\(^{-1}\), and 552 cm\(^{-1}\), as shown in Figure 3b. The broadband observed at 3396 cm\(^{-1}\) is due to the –OH stretching modes and the peaks at 1605 cm\(^{-1}\) and 1039 cm\(^{-1}\) indicate the presence of hydroxyl groups associated with Cr\(^{3+}\) ions [10]. The peak at 2920 cm\(^{-1}\) can be assigned to the C–H stretching and bending vibrations [11]. Metal oxides, generally, exhibit absorption bands around 1000 cm\(^{-1}\) as a result of inter-atomic vibrations. Hence, the weak band around 1039 cm\(^{-1}\) is due to Cr=O vibration modes, and the band at 552 cm\(^{-1}\) is the characteristic stretching bonds of Cr-O-Cr, which indicate the presence of hexagonal Cr\(_2\)O\(_3\) nanostructure [10].

![Figure 3. FTIR spectra of (a) V. amygdalina leaf extract and (b) synthesized Cr\(_2\)O\(_3\) nanostructures.](image)

3.3. Scanning electron microscopy (SEM).

The morphological studies of Cr\(_2\)O\(_3\) nanostructures synthesized using *V. amygdalina* leave extracts were analyzed by scanning electron microscopy, SEM model JSM-IT300LV, in the micrometer scale. SEM images of the samples are shown in Figure 4 below. The images of the as-synthesized nanostructures revealed that it is granular in structure.

![Figure 4. SEM images of Cr\(_2\)O\(_3\) nanostructures synthesized from *V. amygdalina* leaf extracts.](image)
4. Conclusions

In summary, a simple, cost-effective, and eco-friendly biological technique was employed for the successful synthesis of Cr$_2$O$_3$ nanostructures using CrCl$_3$•6H$_2$O as a precursor, and aqueous extract of V. amygdalina leaves as a reducing and stabilizing agent under low-temperature condition. The mean crystallite size was 23.4 nm, as confirmed from the detailed analysis of XRD patterns using the Scherrer equation. Rietveld refinement of XRD spectra also confirmed that Cr$_2$O$_3$ was dominantly observed in the pattern with minor existence of CrO$_2$ peaks as an impurity. V. amygdalina leaf extract is, therefore, a good reducing and stabilizing agent for the synthesis of Cr$_2$O$_3$ nanostructures. The as-synthesized Cr$_2$O$_3$ nanostructures were also stable, and this shows that the synthesis method is reproducible for large scale production.

Funding

This research received no external funding.

Acknowledgments

The researchers would like to express their heartfelt gratitude to the Materials Science and Engineering Department at Addis Ababa Science and Technology University for running SEM characterization and Chemistry Department at Addis Ababa University for FTIR characterization. The researchers are also thankful to the Materials Science and Engineering Department at Addama Science and Technology University for running XRD characterization.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Sousa, P.; Silvestre, A.J.; Conde, O. Cr2O3 thin films grown at room temperature by low pressure laser chemical vapour deposition. Thin Solid Films 2011, 519, 3653-3657, https://doi.org/10.1016/j.tsf.2011.01.382.
2. Shu-ting Liang, H.-I.Z., Min-ting Luo, Ke-jun Luo, Ping Li, Hong-bin Xu, Yi Zhang. Colour performance investigation of a Cr2O3 green pigment prepared via the thermal decomposition of CrOOH. Ceram. Int. 2014, 40, 4367-4373, https://doi.org/10.1016/j.ceramint.2013.08.107.
3. Sangeetha, S.; Basha, R.; Sreram, K.J.; Sangilimuthu, S.N.; Nair, B.U. Functional pigments from chromium (III) oxide nanoparticles. Dyes Pigm. 2012, 94, 548-552, https://doi.org/10.1016/j.dyepig.2012.03.019.
4. Pang, X.; Gao, K.; Volinsky, A.A. Microstructure and mechanical properties of chromium oxide coatings. J. Mater. Res. 2007, 22, 3531-3537, https://doi.org/10.1557/JMR.207.0445.
5. Zhang, Y.; Li, J.; Huang, J.; Ding, C. Mechanical and tribological properties of plasma-sprayed Cr 3 C 2-NiCr, WC-Co, and Cr 2 O 3 coatings. J. Therm. Spray Technol. 1998, 7, 242-246, https://doi.org/10.1361/105996398770359881.
6. Celik, E.; Tekmen, C.; Ozdemir, I.; Cetinel, H.; Karakas, Y.; Okumus, S. Effects on performance of Cr2O3 layers produced on Mo/cast-iron materials. Surf. Coat. Technol. 2003, 174, 1074-1081.
7. El-Sheikh, S.; Mohamed, R.; Fouad, O. Synthesis and structure screening of nanostructured chromium oxide powders. J Alloy Compd 2009, 482, 302-307, https://doi.org/10.1016/j.jallcom.2009.04.011.
8. Gibot, P.; Vidal, L. Original synthesis of chromium (III) oxide nanoparticles. J Eur Ceram Soc 2010, 30, 911-915, https://doi.org/10.1016/j.jeurceramsoc.2009.09.019.
9. Li, L.; Yan, Z.F.; Lu, G.Q.; Zhu, Z.H. Synthesis and structure characterization of chromium oxide prepared by solid thermal decomposition reaction. J Phys Chem B 2006, 110, 178-183, https://doi.org/10.1021/jp053810b.
11. Li, L.; Zhu, Z.; Yao, X.; Lu, G.; Yan, Z. Synthesis and characterization of chromium oxide nanocrystals via solid thermal decomposition at low temperature. *Microporous Mesoporous Mater.* 2008, 112, 621-626, https://doi.org/10.1016/j.micromeso.2007.10.044.

12. Zhao, W.; Jiang, H.; Liu, J.; Deng, X.; Bi, Y.; Zhang, S. Preparation of Cr2O3 nanoparticles via surfactant-modified precipitation method and their catalytic effect on nitridation of silicon powders. *J Ceram Soc Jpn* 2017, 125, 623-627, https://doi.org/10.2109/jcersj2.17047.

13. Pei, Z., Zhang, Y. A novel method to prepare Cr2O3 nanoparticles. *Mater. Lett.* 2008, 62, 504-506, https://doi.org/10.1016/j.matlet.2007.05.073.

14. Pei, Z.; Xu, H.; Zhang, Y. Preparation of Cr2O3 nanoparticles via C2H5OH hydrothermal reduction. *J Alloy Compd* 2009, 468, L5-L8, https://doi.org/10.1016/j.jallcom.2007.12.086.

15. Fu, X.-Z.L., Xiao-Xiong Luo, Jing-Li Chuang, Karl T. Sanger, Alan R. Krzywicki, Andrzej. Ethane dehydrogenation over nano-Cr2O3 anode catalyst in proton ceramic fuel cell reactors to co-produce ethylene and electricity. *J. Power Sources* 2011, 196, 1036-1041, https://doi.org/10.1016/j.jpowsour.2010.08.043.

16. Lima, M.; Bonadimann, R.; de Andrade, M.; Bergmann, C. Nanocrystalline Cr2O3 and amorphous CrO3 produced by solution combustion synthesis. *J Eur Ceram Soc* 2006, 26, 1213-1220, https://doi.org/10.1016/j.jeurceramsoc.2005.01.042.

17. Ramesh, C.; Mohan Kumar, K.; Latha, N.; Raganathan, V. Green synthesis of Cr2O3 nanoparticles using Tridax procumbens leaf extract and its antibacterial activity on Escherichia coli. *Curr Nanoscience* 2012, 8, 603-607, https://doi.org/10.2174/157341312801784366.

18. Habtemariam, A.B.; Sibhatu, A.K.; Weldegebriel, G.K.; Zelezkiew, O.A.; Tekletsadik, B.T. Bio-mediated synthesis of ZnO nanostructures from Thymus Schimperi leaves extract and its antibacterial and photocatalytic activities. *Lett Appl NanoBioSci* 2020, 9, 808-813.

19. Mittal, A.K.; Chisti, Y.; Banerjee, U.C. Synthesis of metallic nanoparticles using plant extracts. *Biotechnol. Adv.* 2013, 31, 346-356, https://doi.org/10.1016/j.biotechadv.2013.01.003.

20. Abosi, A.O.; Raseroika, B.H. In vivo antimarial activity of Vernonnia amygdalina. *Br J Biomed Sci* 2003, 60, 89-91, https://doi.org/10.1080/09674845.2003.11783680.

21. Farombi, E.O.; Owoseye, O. Antioxidative and chemopreventive properties of Vernonnia amygdalina and Garcinia biflavonoid. *Int J Environ Res Publ Health* 2011, 8, 2533-2555, https://doi.org/10.3390/ijerph8062533.

22. Erasto, P.; Grierson, D.; Afolayan, A. Antioxidant constituents in Vernonnia amygdalina Leaves. *Pharm Biol* 2007, 45, 195-199, https://doi.org/10.1080/13880200701213070.

23. Mekoya, A.; Oosting, S.J.; Fernandez-Rivera, S.; Van der Zijpp, A. Multipurpose fodder trees in the Ethiopian highlands: Farmers’ preference and relationship of indigenous knowledge of feed value with laboratory indicators. *Agricultural Systems* 2008, 96, 184-194, https://doi.org/10.1016/j.agsy.2007.08.001.

24. Atangwho, I.; Epong, P.; Eyong, E.; Williams, I.; Eten, M.; Egbung, G. Comparative chemical composition of leaves of some antidiabetic medicinal plants: Azadirachta indica, Vernonnia amygdalina and Gongronema latifolium. *African Journal of Biotechnology* 2009, 8.

25. Habtemariam, A.B.; Oumer, M. Plant Extract Mediated Synthesis of Nickel Oxide Nanoparticles. *Mater Int* 2020, 2, 205-209, https://doi.org/10.33263/Materials22.205209.

26. Ahmed Mohamed, H.E.; Afredis, S.; Khalil, A.T.; Zohra, T.; Ali, M.; Alam, M.M.; Ikram, A.; Shinwari, Z.K.; Maaza, M. Phyto-fabricated Cr2O3 nanoparticle for multifunctional biomedical applications. *Nanomedicine* 2020, 15, 1653-1669, https://doi.org/10.2217/nmm-2020-0129.

27. Iqbal, J.; Abbasi, B.A.; Munir, A.; Uddin, S.; Kanwal, S.; Mahmood, T. Facile green synthesis approach for the production of chromium oxide nanoparticles and their different in vitro biological activities. *Microscopy Research and Technique* 2020, 83, 706-719, https://doi.org/10.1002/jemt.23460.

28. Aisida, S.O.; Madubuonu, N.; Alnasir, M.H.; Ahmad, I.; Botha, S.; Maaza, M.; Ezema, F.I. Biogenic synthesis of iron oxide nanorods using Moringa oleifera leaf extract for antibacterial applications. *Applied Nanoscience* 2020, 10, 305-315, https://doi.org/10.1007/s13204-019-01099-x.