Nanochem Res 6(1): 18-24, Winter and Spring 2021

RESEARCH PAPER

Structural, Optical and Magnetic Studies of Cr_2O_3 Nanoparticles Prepared by Microwave-Assisted Synthesis

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ARTICLE INFO

Article History:
Received 15 December 2020
Accepted 23 February 2021
Published 15 March 2021

Keywords:
Cr_2O_3 nanoparticles
Quasi-rectangular
Microwave-assisted
Ferromagnetic

ABSTRACT

In this paper, quasi-rectangular Cr_2O_3 nanoparticles were prepared by microwave-assisted solution synthesis using $Cr(NO_3)_2.6H_2O$ and salicylic acid at the presence of NaOH in optimum conditions for the power of 360 W, the temperature of 50 °C, and the time duration of 30 min. The as-prepared chromium precursor was annealed in an air atmosphere at two different temperatures, 500 and 600 °C, for 3 h. Quasi-rectangular Cr_2O_3 nanoparticles were prepared and characterized by Fourier transform infrared (FT-IR), ultraviolet–visible (UV-Vis) spectroscopy, X-ray diffraction analysis (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). The sharp peaks in FT-IR spectra and high intensity peaks in XRD patterns confirm the existence of a single and pure phase of the Cr_2O_3 nanoparticles with an average nanoparticle size of 25 nm. The calculated optical band gap (Eg) values of the as-prepared Cr_2O_3 nanoparticles were in the range of 1.6 and 1.8 eV. The TEM images revealed a highly homogeneous quasi-rectangular morphology without any agglomeration. The magnetic properties of the Cr_2O_3 nanoparticles showed weak ferromagnetic behavior.

How to cite this article
Dehno Khalaji A.A. Structural, Optical and Magnetic Studies of Cr_2O_3 Nanoparticles Prepared by Microwave-Assisted Synthesis . Nanochem Res, 2021; 6(1):18-24. DOI: 10.22036/ncr.2021.01.003

INTRODUCTION

Chromium (III) oxide (Cr_2O_3) is one of the most important transition metal oxide because of its good catalytic, magnetic, electrical and gas sensing properties as well as being one of the most stable pigments [1-12]. In addition, Cr_2O_3 nanoparticles have high mechanical and physicochemical properties with a wide band gap ($E_g \approx 3.4$ eV) [13-15]. There are many methods to prepare Cr_2O_3 nanoparticles such as sol-gel, microwave, hydro- and solvo-thermal, thermal decomposition, combination membrane, pulse laser deposition, mechano-chemical and casting methods [1-12, 16-18]. Microwave-assisted synthesis is a new technique for the synthesis of various transition metal oxide nanoparticles. Recently, it is being of interest as an appropriate tool due to its short duration, highly pure nanoparticles preparation, and improved physico-chemical properties [1, 6, 19, 20]. Recent studies have shown problems for the production of Cr_2O_3 nanoparticles such as morphology control, purity and high thermal stability [21]. Yahyazadehfar *et al.* [22] prepared Cr_2O_3 nanoparticles using microwave-assisted synthesis in optimum conditions with highly homogeneous morphology of crystalline nanostructures, existence of single phase, high thermal stability and high specific surface. Deppak *et al.* [1] prepared Cr_2O_3 nanoparticles using $Cr(acac)_3$ and ethylene glycol by microwave-assisted synthesis in high yield (95%). Su *et al.* [6] prepared spherical Cr_2O_3 nanoparticles using K_2CrO_4 as a precursor by microwave-assisted synthesis.

In this paper, continuing the previous work

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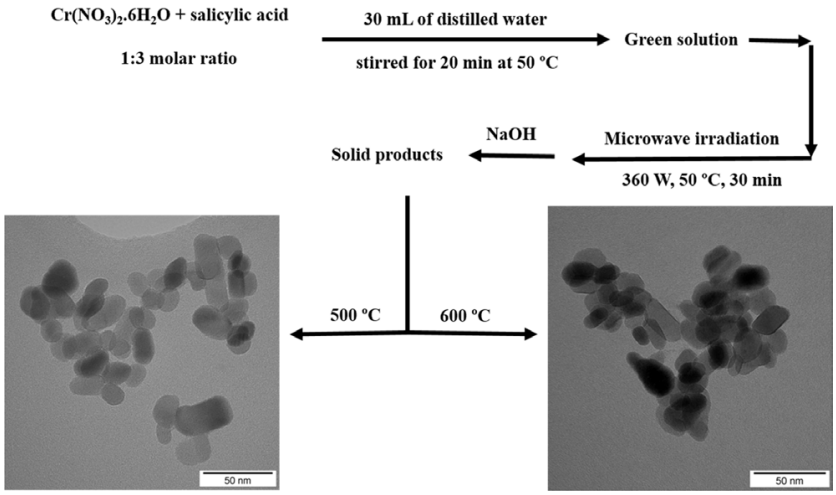

Scheme 1. Schematic of the synthetic route for quasi-rectangular Cr_2O_3 nanoparticles

on the transition metal nanoparticles [23-28], Cr_2O_3 nanoparticles with quasi-rectangular shape (Scheme 1) were synthesized by microwave-assisted solution synthesis as an-easy-to-use and effective method. The Cr_2O_3 nanoparticles were then characterized by FT-IR, UV-Vis, XRD, TEM and VSM.

EXPERIMENTAL

Materials and Methods

$Cr(NO_3)_2.6H_2O$, salicylic acid and NaOH were purchased from Merck company and used without further purification. FT-IR and UV-Vis spectra were carried out using a Perkin-Elmer and Jasco spectrophotometer, respectively. The X-ray patterns were conducted with a Bruker AXS diffractometer D8 ADVANCE in the range $2\theta = 10^o–80^o$. TEM images were recorded on transmission electron microscope Philips with CCD camera Olympus Veleta. The magnetic properties were investigated by Vibrating sample magnetometer.

Synthesis of Cr_2O_3 nanoparticles

A mixture of $Cr(NO_3)_2.6H_2O$ and salicylic acid (1:3 molar ratio) were dissolved into 30 mL of distilled water and stirred for 20 min at 50 °C. Then the solution was located under microwave irradiation at optimized conditions (the power of 360 W, temperature of 50 °C, and time duration of 30 min). An aqueous solution of NaOH was added dropwise to this solution until the pH reached 12. After cooling to r.t. the solid products were obtained by decanting, and were dried at 100 °C. Then they were divided into two equal parts and heated at the temperatures of 500 and 600 °C for 3 h. After that, the as-prepared Cr_2O_3 nanoparticles with quasi-rectangular shape were washed twice with distilled water and being dried at 80 °C in a furnace for 24 h. Finally, the products were characterized by FT-IR, UV-Vis, XRD, TEM and VSM.

RESULTS AND DISCUSSION

FT-IR and UV-Vis spectra

FT-IR spectra of the Cr_2O_3 nanoparticles prepared at 500 and 600 °C are shown in Fig. 1. Two weak and sharp absorption bands at about 410 and 442 cm^{-1} and two strong and sharp absorption bands at 555 and 620 cm^{-1} confirmed the Cr-O single bonds [29-31]. The first three bands at 410, 442, and 555 cm^{-1} can be attributed to the bending mode of Cr-O and the band at 620 cm^{-1} confirmed the presence of crystalline α-Cr_2O_3 [32]. The high intensity of the peaks of Cr_2O3 bands indicates the good crystalline nature of the α-Cr_2O_3 materials [33]. The weak broad band at about 1626 cm^{-1} may be attributed to the presence of water molecules adsorbed at the surface of the α-Cr_2O_3 nanoparticles [29].The relatively strong broad band at 3398 cm^{-1} for the as-prepared Cr_2O_3 nanoparticles at 500 °C and 3424 cm^{-1} for the as-prepared Cr_2O_3 nanoparticles at 600 °C confirmed the O-H stretching mode of water molecules [29]. The other band at 950 cm^{-1} is due to the combination of lattice modes [34].

UV-Vis spectra of the Cr_2O_3 nanoparticles prepared at 500 and 600 °C are shown in Fig. 2.

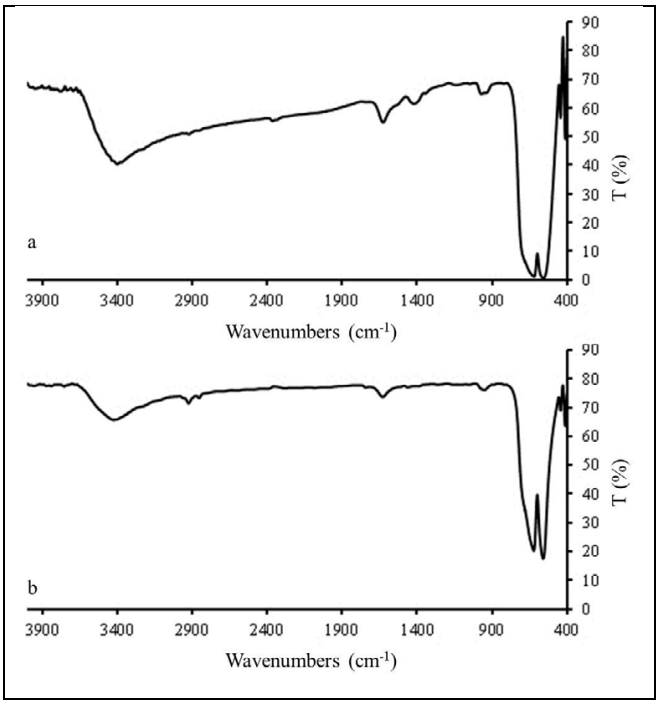

Fig. 1. FT-IR spectra of the as-prepared Cr_2O_3 nanoparticles at a) 500 °C and b) 600 °C

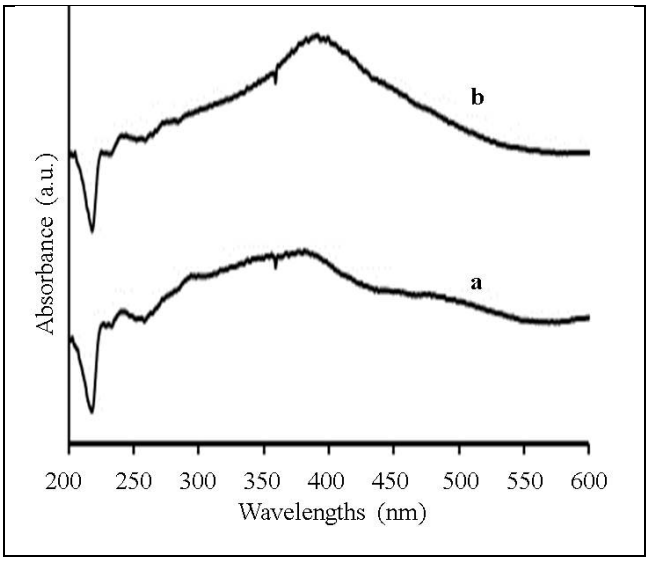

Fig. 2. UV-Vis spectra of the as-prepared Cr_2O_3 nanoparticles at a) 500 °C and b) 600 °C

A broad absorption peak appeared at about 390 nm and confirmed the d^3 electronic transition of Cr^{3+} ion in the six coordination geometry and octahedral symmetry, corresponding to the $^4A_{2g} \rightarrow {}^4T_{1g}$ [9, 34]. However, a weak shoulder at about 480 nm appeared for the Cr_2O_3 nanoparticles prepared at 500 °C. The optical band gap 'E_g' of the as-prepared Cr_2O_3 nanoparticles was calculated using Tauc's equation [13, 35]:

$(\alpha h\upsilon)^2 = A(h\upsilon - Eg)$

Where A is a constant; α is the absorption coefficient; hυ is the photon energy and E_g is the optical band gap energy. The energy band gap of 1.6 and 1.8 eV for the Cr_2O_3 nanoparticles prepared

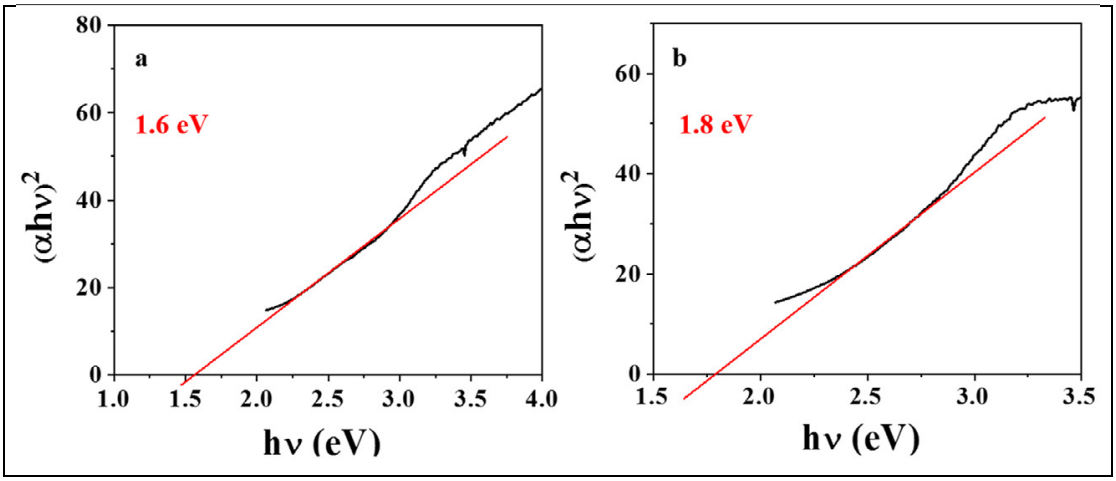

Fig. 3. Tauc plot obtained UV-Vis spectra of the as-prepared Cr_2O_3 nanoparticles at a) 500 °C and b) 600 °C

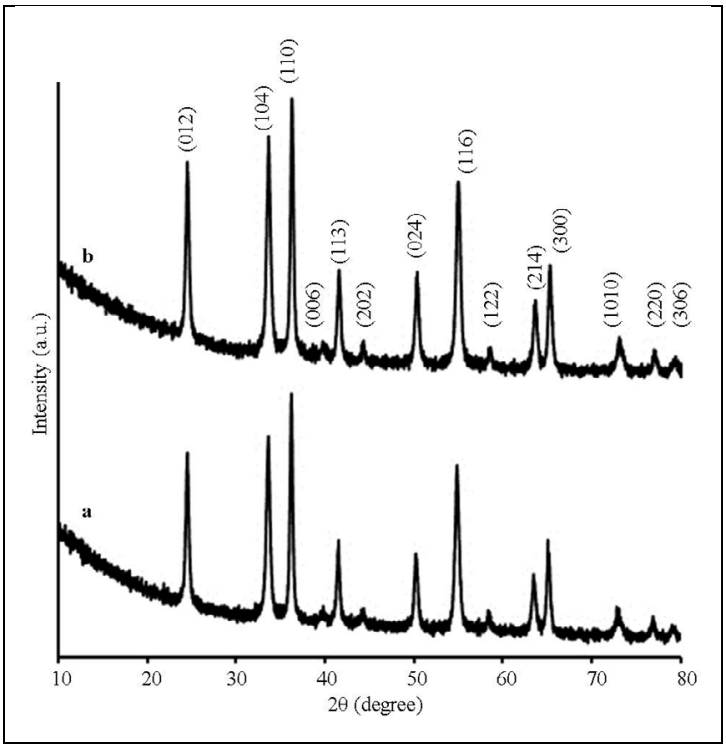

Fig. 4. XRD patterns of the as-prepared Cr_2O_3 nanoparticles at a) 500 °C and b) 600 °C

at 500 and 600 °C have been determined using the results of UV-Vis spectrophotometer (Fig. 3) which are lower than those reported by several authors [35, 36].

XRD patterns

Fig. 4 shows the XRD patterns of the as-prepared Cr_2O_3 nanoparticles at 500 and 600 °C. It can be seen that the diffraction peaks were indexed in the rhombohedral structure with an R-3c space group and could be indexed to those of pure Cr_2O_3 (JCPDS card # 38-1479) [3-8, 10, 21]. The peak broadening of the patterns confirmed very small crystallines which according to Scherrer's equation and the sharp peak appeared at $2\theta \approx 37$ (110), the average crystalline size is 20 nm.

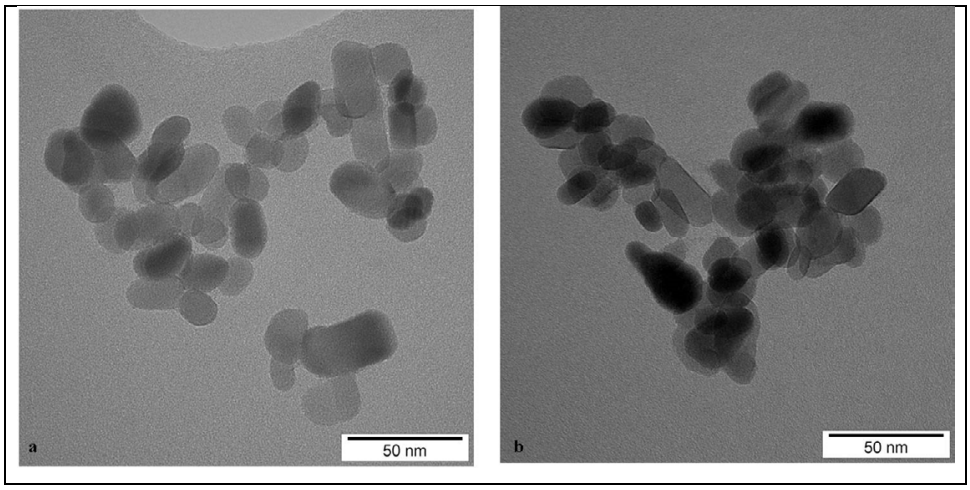

Fig. 5. TEM images of the as-prepared Cr_2O_3 nanoparticles at a) 500 °C and b) 600 °C

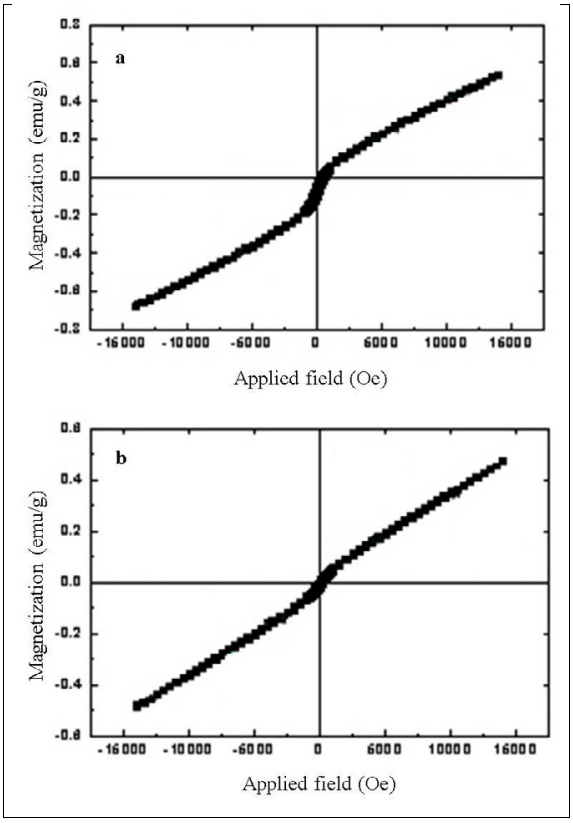

Fig. 6. VSM of the as-prepared Cr_2O_3 nanoparticles at a) 500 °C and b) 600 °C

TEM images

Fig. 5 demonstrates the TEM images of the as-prepared Cr_2O_3 nanoparticles at 500 and 600 °C. The images show that Cr_2O_3 nanoparticles mainly exhibit quasi-rectangular shape (minimum 10 and maximum 40 nm) and almost uniform in size and shape. When the temperature decomposition was increased to 600°C, the as-prepared Cr_2O_3 nanoparticles became agglomerated.

VSM

The magnetic properties of the as-prepared Cr_2O_3 nanoparticles at 500 and 600 °C were studied as a function of applied magnetic field and shown

in Fig. 6. It was observed that the M *vs*. H graph is linear and no saturation magnetization can be seen even at high magnetic field [9, 11, 12], indicating paramagnetic behavior while bulk Cr_2O_3 is antiferromagnetic [12].

CONCLUSION

Quasi-rectangular Cr_2O_3 nanoparticles were synthesized and characterized. FT-IR and XRD results confirmed the single-phase existence and purity of Cr_2O_3 with the rhombohedral structure. The particle size was examined by TEM and indicated the nanosize of the samples. The average size of the sample is about 20 nm. The magnetic measurement indicated the paramagnetic nature of the as-prepared quasi-rectangular Cr_2O_3 nanoparticles.

ACKNOWLEDGMENTS

This work was supported by Golestan University.

CONFLICTS OF INTEREST

The authors announce that there are no conflicts of interest.

REFERENCES

1. Deepak HN, Choudhari KS, Shivashankar SA, Santhosh C, Kulkarni SD. Facile microwave-assisted synthesis of Cr2O3 nanoparticles with high near-infrared reflection for rooftop cooling applications. Journal of Alloys and Compounds. 2019;785:747-53.
2. Golosova NO, Kozlenko DP, Kichanov SE, Lukin EV, Liermann HP, Glazyrin KV, et al. Structural and magnetic properties of Cr2O3 at high pressure. Journal of Alloys and Compounds. 2017;722:593-8.
3. Pei Z, Pei J, Chen H, Gao L, Zhou S. Hydrothermal synthesis of large sized Cr2O3 polyhedrons under free surfactant. Materials Letters. 2015;159:357-61.
4. Sun H, Wang L, Chu D, Ma Z, Wang A. Synthesis of porous Cr2O3 hollow microspheres via a facile template-free approach. Materials Letters. 2015;140:35-8.
5. Xu X, Wu J, Yang N, Na H, Li L, Gao J. Cr2O3: a novel supercapacitor electrode material with high capacitive performance. Materials Letters. 2015;142:172-5.
6. Su J, Xue H, Gu M, Xia H, Pan F. Synthesis of spherical Cr2O3 nanoparticles by a microwave refluxing method and their photocatalytic properties. Ceramics International. 2014;40(9):15051-5.
7. Zhang HL, Liang ST, Luo MT, Ma MG, Fan PP, Xu HB, et al. Preparation and color performance control of Cr2O3 green pigment through thermal decomposition of chromium hydroxide precursor. Materials Letters. 2014;117:244-7.
8. Pei Z, Zhang X. Controlled synthesis of large-sized Cr2O3 via hydrothermal reduction. Materials Letters. 2013;93:377-9.
9. Anandan K, Rajendran V. Studies on structural, morphological, magnetic and optical properties of chromium sesquioxide (Cr2O3) nanoparticles: Synthesized via facile solvothermal process by different solvents. Materials Science in Semiconductor Processing. 2014;19:136-44.
10. Gunnewiek RFK, Mendes CF, Kiminami RHGA. Synthesis of Cr2O3 nanoparticles via thermal decomposition of polyacrylate/chromium complex. Materials Letters. 2014;129:54-6.
11. Tüysüz H, Weidenthaler C, Grewe T, Salabaş EL, Benitez Romero MJ, Schüth F. A Crystal Structure Analysis and Magnetic Investigation on Highly Ordered Mesoporous Cr2O3. Inorganic Chemistry. 2012;51(21):11745-52.
12. Gupta RK, Mitchell E, Candler J, Kahol PK, Ghosh K, Dong L. Facile synthesis and characterization of nanostructured chromium oxide. Powder Technology. 2014;254:78-81.
13. Abdullah MM, Rajab FM, Al-Abbas SM. Structural and optical characterization of Cr2O3 nanostructures: Evaluation of its dielectric properties. AIP Advances. 2014;4(2):027121.
14. Sadri E, Ashrafizadeh F. Structural characterization and mechanical properties of plasma sprayed nanostructured Cr2O3-Ag composite coatings. Surface and Coatings Technology. 2013;236:91-101.
15. Jawaher KR, Indirajith R, Krishnan S, Robert R, Pasha SKK, Deshmukh K, et al. A High Sensitivity Isopropanol Vapor Sensor Based on Cr2O3–SnO2 Heterojunction Nanocomposites via Chemical Precipitation Route. Journal of Nanoscience and Nanotechnology. 2018;18(8):5454-60.
16. Tsuzuki T, McCormick PG. Synthesis of Cr2O3 nanoparticles by mechanochemical processing. Acta Materialia. 2000;48(11):2795-801.
17. Khamlich S, Nuru ZY, Bello A, Fabiane M, Dangbegnon JK, Manyala N, et al. Pulsed laser deposited Cr2O3 nanostructured thin film on graphene as anode material for lithium-ion batteries. Journal of Alloys and Compounds. 2015;637:219-25.
18. Yu S, Wang B, Pan Y, Chen Z, Meng F, Duan S, et al. Cleaner production of spherical nanostructure chromium oxide (Cr2O3) via a facile combination membrane and hydrothermal approach. Journal of Cleaner Production. 2018;176:636-44.
19. Schütz MB, Xiao L, Lehnen T, Fischer T, Mathur S. Microwave-assisted synthesis of nanocrystalline binary and ternary metal oxides. International Materials Reviews. 2017;63(6):341-74.
20. Kato K, Vaucher S, Hoffmann P, Xin Y, Shirai T. A novel single-mode microwave assisted synthesis of metal oxide as visible-light photocatalyst. Materials Letters. 2019;235:125-8.
21. Gibot P. Templated synthesis of Cr2O3 material for energetic composites with high performance. Solid State Sciences. 2019;94:162-7.
22. Yahyazadehfar M, Ahmadi SA, Sheikhhosseini E, Ghazanfari D. High-yielding strategy for microwave-assisted synthesis of Cr2O3 nanocatalyst. Journal of Materials Science: Materials in Electronics. 2020;31(14):11618-23.
23. Khalaji AD. Preparation and Characterization of ZnO Nanoparticles via Thermal Decomposition from Zinc(II) Schiff Base Complex as New Precursor. Chemical Methodologies. 2019;3(5):635-43.
24. Dehno Khalaji A. Synthesis, Characterization and Optical Properties of Co_3O_4 Nanoparticles. Asian Journal of Nanosciences and Materials. 2019;2(2):186-90.
25. Khalaji AD, Jarosova M, Machek P. The Preparation, structural characterization, optical properties, and antibacterial activity of the CuO/Cu_2O nanocomposites prepared by the

facile thermal decomposition of a new copper precursor. Nanomedicine Journal. 2020;7(3):231-6.
26. Dehno Khalaji a. Cr_2O_3 Nanoparticles: Synthesis, Characterization, and Magnetic Properties. Nanochemistry Research. 2020;5(2):148-53.
27. Dehno Khalaji A, Ghorbani M. Thermal Studies of Iron (II) Schiff Base Complexes: New Precursors for Preparation of α-Fe2O3 Nanoparticles via Solid-State Thermal Decomposition. Chemical Methodologies. 2020;4(4):532-42.
28. Dehno Khalaji A, Palang Sangdevini Z, Mousavi SM, Jarosova M, Machek P. Benzoic acid-functionalized α-Fe_2O_3 nanoparticles: synthesis, characterization, magnetic and optical properties. Asian Journal of Nanosciences and Materials. 2021;4(2):137-46.
29. Sone BT, Manikandan E, Gurib-Fakim A, Maaza M. Single-phase α-Cr2O3 nanoparticles' green synthesis using Callistemon viminalis' red flower extract. Green Chemistry Letters and Reviews. 2016;9(2):85-90.
30. Tian S, Ye X, Dong Y, Li W, Zhang B, Li B, et al. Production and Characterization of Chromium Oxide (Cr_2O_3) via a Facile Combination of Electrooxidation and Calcination. Int J Electrochem Sci. 2019;14:8805-18.
31. Salehi M GF. Preparation of chromium(III) oxide sub-micron powders by solid state method without fuel. Applied Chemistry 2015;9(32):97-100.
32. Henderson MA. Photochemistry of methyl bromide on the α-Cr2O3(0001) surface. Surface Science. 2010;604(19-20):1800-7.
33. Madi C, Tabbal M, Christidis T, Isber S, Nsouli B, Zahraman K. Microstructural characterization of chromium oxide thin films grown by remote plasma assisted pulsed laser deposition. Journal of Physics: Conference Series. 2007;59:600-4.
34. Roy M, Ghosh S, Naskar MK. Solvothermal synthesis of Cr2O3 nanocubes via template-free route. Materials Chemistry and Physics. 2015;159:101-6.
35. Zekaik A, Benhebal H, Benrabah B. Synthesis and characterization of Cu doped chromium oxide (Cr2O3) thin films. High Temperature Materials and Processes. 2019;38(2019):806-12.
36. Hu Z, Xu M, Shen Z, Yu JC. A nanostructured chromium(iii) oxide/tungsten(vi) oxide p–n junction photoanode toward enhanced efficiency for water oxidation. Journal of Materials Chemistry A. 2015;3(26):14046-53.