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Synthesis and Structural Characterization of $ZnCr_2O_4$ Nano Particles Prepared by Citrate-gel Auto Combustion Method

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Zinc chromite nano particles (NPs) have been synthesized via Citrate-gel auto combustion method using citric acid as chelating agent. Structural characterization of the prepared sample was carried out using X-ray diffraction analysis, FESEM and EDS analysis, dynamic light scattering (DLS) analysis and FTIR spectroscopic analysis. XRD analysis confirms the formation spinel oxide with a crystallite size of 36 nm as calculated using Debye-scherrer's formula. FTIR studies also confirm the formation of spinel structure. Structural morphology was studied by field emission scanning electron microscopy that indicates the presence of globule shaped particles. EDS images show the presence of only Zn, Cr and O without any other impurity elements. This fact confirms the purity of the prepared nano particles. Average particles size of the prepared sample was 20 nm as measured by DLS technique.

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Keywords: Zinc chromite nano particles; citrate-gel auto combustion method; XRD; FESEM & EDS analysis; DLS and FTIR analysis.

1. INTRODUCTION

Mixed spinel oxides are complex metal oxides and have been an area of extensive study in recent years due to their significance in magnetic materials [1], catalysts [2], luminescence materials [3], sensors [4], lithium batteries [5] etc. Mixed spinel oxides are represented by the chemical formula AB_2O_4 where *A*-denotes divalent cations occupying tetrahedral sites and *B*-denotes trivalent cations in octahedral sites [6]. Now a days, spinel oxides with the chemical formula MCr_2O_4 (where M stands for metal such as Zn, Cu, Co, Mg, Ni Fe etc.) has been the interest of many researchers because of their extraordinary properties [7]. These materials in nanoscale are significant due to their small size and large surface area and exhibit improved properties than normal materials. $ZnCr_2O_4$ mixed spinels are of important functional materials because of its wide range of applications as humidity sensor [8], photocatalyst [9], catalytic material for a variety of reactions such as oxidation, hydrogenation and steam reforming [10], and magnetic material [11]. Properties of the material depend on the method of synthesis and reaction conditions. Many synthesis methods were reported earlier for the synthesis of $ZnCr_2O_4$ such as solid state reaction method [12], ball milling [13], micro emulsion method [14], solution method [15], co-prepcipitation method [16] etc. Some of these techniques prepare the product of low quality with presence of impurities, some require high temperature, consume more energy require organic solvents for the synthesis which make the process costly. Present paper reports the synthesis of $ZnCr_2O_4$ NPs via citrate-gel auto combustion method using citric acid as chelating agent. The purpose of selecting this method is simple, low cost, and prepares the material of high purity, good homogeneity at low processing temperature.

2. MATERIALS AND METHODS

Zinc nitrate, chromium nitrate, citric acid, ammonia solution of analytical grade were used as starting materials for the synthesis of $ZnCr_2O_4$ NPs via citrate-gel auto combustion method.

2.1 Synthesis of $ZnCr_2O_4$ NPs Via Citrate-gel Auto Combustion Method

Aqueous solutions of metal nitrates were prepared and mixed. To this solution citric acid solution was added and resulting mixture is kept on magnetic stirrer. The solution was thoroughly stirred on the stirrer to get a homogeneous solution and then ammonia solution was added to adjust the pH of the solution to 7 by slightly increasing the temperature to 100°C. Slowly the water evaporates and the temperature is further increased. On complete evaporation of water from the mixture, the solution turns into gel. This on further heating undergoes self ignition and starts burning in the hottest portion of the beaker at the bottom and undergoes complete combustion resulting in the formation of a loose puffy mass. This was ground in mortar and pestle to result in a fine powder reported as $ZnCr_2O_4$ powder. This was subjected to calcination in muffle furnace at 500°C for four hours. The resulting calcinated powder is subjected to structural characterization using various techniques.

2.2 Characterization Techniques

The prepared sample was subjected to X-ray diffraction analysis for the phase confirmation and particle size determination using X-ray diffractometer (Bruker AXS D8 Advance with Cu Kα radiation in the 2θ range of 20–80 Degrees). The surface morphology was studied by field emission scanning electron microscopy & energy dispersive spectroscopy (FESEM & EDS) (XL30). Dynamic light scattering (DLS) (Horiba SZ100) was performed on samples suspended in ethanol using a YD-laser (532 nm) and the mean value of the obtained histogram was considered the average particle size. Fourier transform infrared spectroscopy (FTIR) (Magna Nicolet 550) was performed for wavelengths 500-3700 cm^{-1} to confirm the spinel formation.

3. RESULTS AND DISCUSSION

Various people have been previously reported on the synthesis, characterization and applications of ZnCr2O4 spinels [17-19]. In this paper, we have made an attempt of synthesis and study of structural characterization of ZnCr2O4 via citrate-gel auto combustion method.

3.1 Structural Analysis of $ZnCr_2O_4$ NPs

X-ray diffraction studies were performed between 2θ values 15° and 75° using Cu Kα (λ=1.5418A°) radiation. The XRD pattern of $ZnCr_2O_4$ powder

was shown in Fig. 1. The observed diffraction patterns were compared with pure $ZnCr_2O_4$ spinel (JCPDS card No. 22-1107) [16]. Each peak having different 2θ positions correspond to different crystalline planes (111), (220), (311), (222), (400), (422), (511), (440) and (533) as compared to standard pattern. Some extra peaks other than standard peaks correspond to small amount of ZnO. The average crystallite sizes for the sample was analyzed from the sharpest peak observed at $2\theta=36^{o}$ by using Debye Scherrer's formula [20].

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where *k* is Debye–Scherer's constant, *β* is the full width half maximum (FWHM) of the XRD corresponding peak, *D* is crystallite size, *λ* is wave length of the X-rays used, *θ* is Bragg's angle. The average size was found to be 36 nm. Hence, XRD study confirms the formation of cubic phased spinel $ZnCr_2O_4$ NPs.

3.2 Morphology and Particle Size Analysis

The morphology of the $ZnCr_2O_4$ NPs was evaluated by FESEM and particle size by dynamic light scattering equipment. FESEM images shown in Fig. 2 indicate appearance of spongy porous like structure with the presence of globule like particles in the sample. The globule shaped particles were confirmed to be $ZnCr_2O_4$ NPs by energy dispersive X-ray spectroscopy provided along with the FESEM. Only Zn, Cr and O elements were detected from EDS patterns as evident from Fig. 3. It is interesting to note that the dynamic light scattering analysis revealed the particle size to be in the range of 20nm as indicated in Fig. 4.

3.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Formation of spinel structured NPs was also confirmed by FTIR analysis. Fig. 4 represents the FTIR spectra of $ZnCr_2O_4$ NPs measured in the wavelength range from 500 to 700 cm^{-1}. The broad absorption peaks observed at low frequency within 500-700 cm^{-1} confirms the vibration of metal-oxygen bonds in spinel structure. The band observed at around 556 cm^{-1} is the characteristic of vibration of Zn-O bond in tetrahedral site where as the band observed at around 632.9 cm^{-1} is the characteristic of vibration of Zn-Cr bonding at the octahedral site in the spinel structure. From the figure it is also clear that peak that observed at 1035.7 cm^{-1} may be due to C-O stretching, peak at 1384.3 cm^{-1} is due to C-C stretching, absorption at 1510.9, 1643.3 $cm^{-}1$ may be due to C=C stretch stretching. The maximum absorption observed between 500 to 700 cm^{-1} confirms the formation of spinel structure of $ZnCr_2O_4$ NPs.

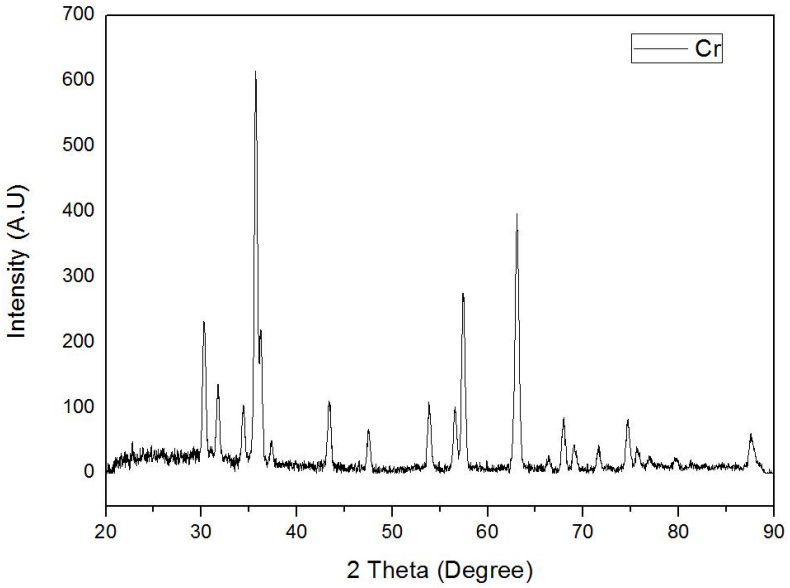

Fig. 1. XRD pattern of $ZnCr_2O_4$

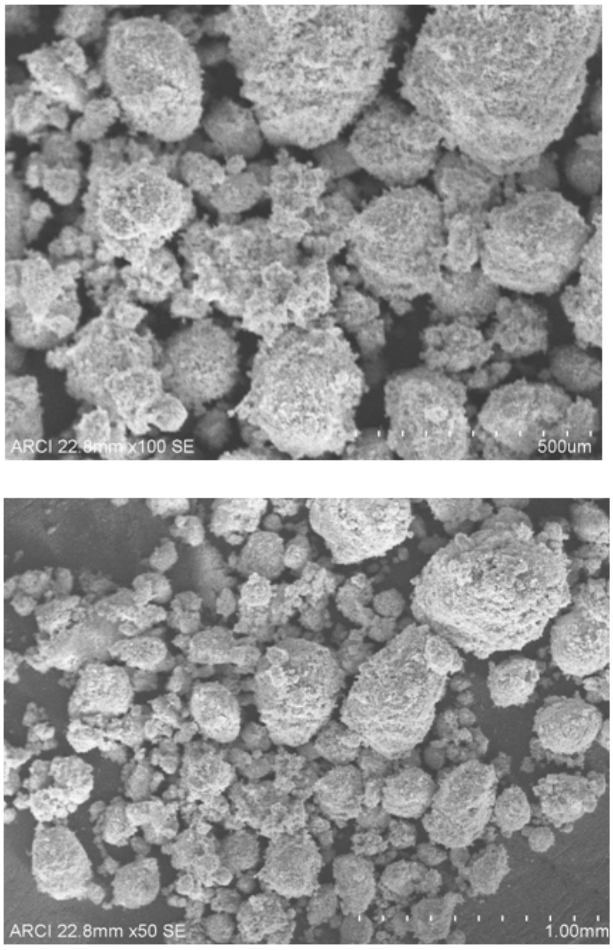

Fig. 2. FESEM Images of ZnCr2O4 NPs

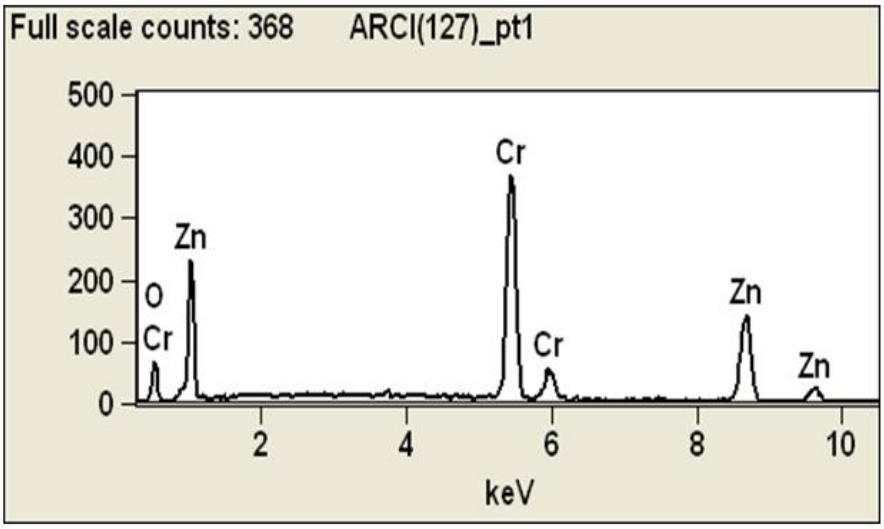

Fig. 3. EDS spectrum of $ZnCr_2O_4$ NPs

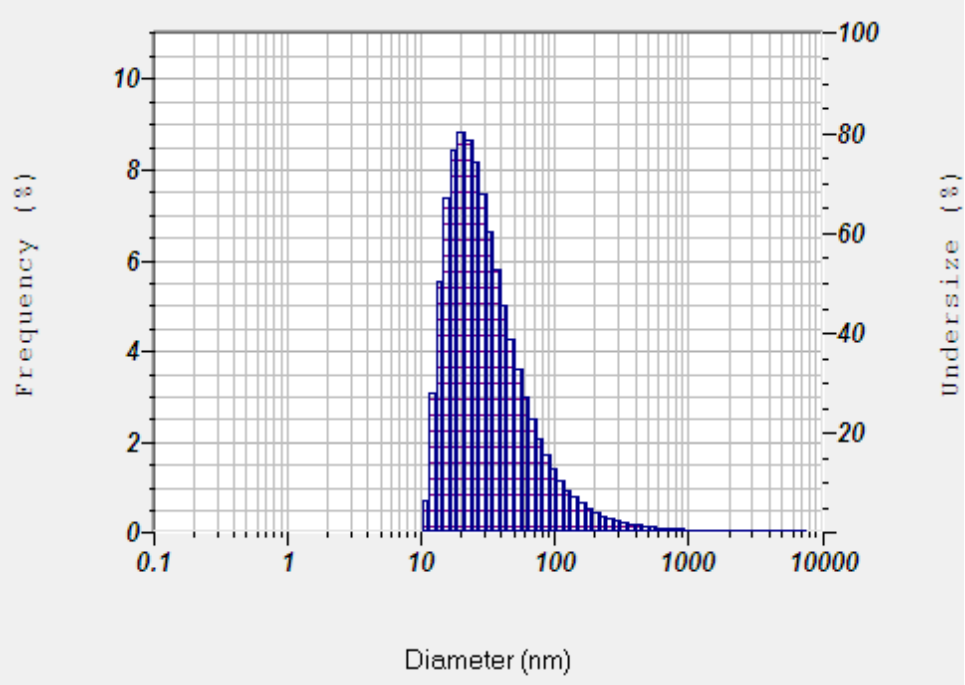

Fig. 4. Particle size distribution of $ZnCr_2O_4$ NPs

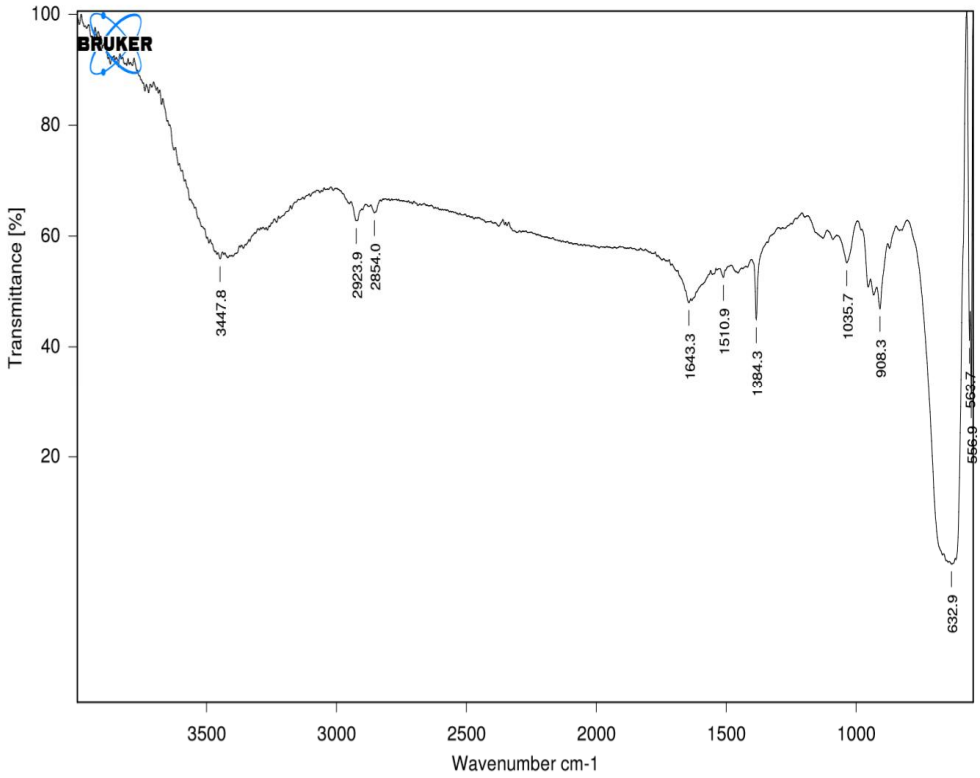

Fig. 5. FTIR spectra of $ZnCr_2O_4$ NPs

4. CONCLUSIONS

$ZnCr_2O_4$ NPs were successfully synthesized using citrate-gel auto combustion method. Formation of cubic spinel structure of prepared $ZnCr_2O_4$ NPs was confirmed by X-ray diffraction analysis and FTIR spectroscopic analysis. In the prepared sample, the particle size measured from FWHM of XRD was observed as 36nm where as the dynamic light scattering analysis revealed the particle size to be in the range of 20 nm. FESEM studies indicated the presence porous network with globule shaped NPs. EDS analysis revealed the purity of prepared sample with the presence of only Zn, Cr and O elements. Average particles size of the prepared sample was 20 nm as measured by DLS technique.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Chinnasamy CN, Narayanasamy A, Ponpandian N, Joseyphus RJ, Chattopadhyay K, Shinoda K, Jeyadevan B, Tohji K, Nakatsuka K, Greneche JM. Ferrimagnetic ordering in nanostructured $CdFe_2O_4$ spinel. Journal of Applied Physics. 2001;90:527–529.
2. Kim DC, Ihm SK. Application of spinel-type cobalt chromite as a novel catalyst for combustion of chlorinated organic pollutants. Environmental Science Technology. 2001;35:222–226.
3. Chaves C, Lima SJG, Araujo RCMU, Maurera MA, Longo E, Pizani PS, Simoes LGP, Soledade LEB, Souza AG, G.d. Santos IM. Photoluminescence in disordered Zn_2TiO_4. Journal of Solid State Chemistry. 2006;179:985–992.
4. Ahn K, Wessels BW, Sampath S. Spinel humidity sensors prepared by thermal spray direct writing. Sensor Actuators B. 2005;107:342–346.
5. Lavela P, Tirado JL, Abarca CV. Sol–gel preparation of cobalt manganese mixed oxides for their use as electrode materials in lithium cells. Electrochimica Acta. 2007; 52:7986–7995.
6. FanY, Lu X, Zhang H, Zhao L, Chen J. Destruction of poly chlorinated aromatic compounds by spinel-type complex oxides. Environmental Science and Technology. 2010;44:3079–84.
7. Shuangming Chen, Yanfei Wu, Peixin Cui, Wangsheng Chu, Xing Chen, Ziyu Wu. Cation distribution in $ZnCr_2O_4$ nanocrystals investigated by X-ray absorption fine structure spectroscopy. Journal of Physical Chemistry C. 2013;117(47):25019–25025.
8. Pokhrel S, Jeyaraj B, Nagaraja KS. Humidity-sensing properties of $ZnCr_2O_4$–ZnO composites. Materials Letters. 2003; 57(22–23):3543–3548.
9. Peng C, Gao L. Optical and photocatalytic properties of spinel $ZnCr_2O_4$ nanoparticles synthesized by a hydrothermal route. Journal of American Ceramic Society. 2008;91(7):2388–2390.
10. Liu N, Yuan Z, Wang C, Wang S, Zhang C, Wang S. The role of CeO_2–ZrO_2 as support in the ZnO–$ZnCr_2O_4$catalysts for autothermal reforming of methanol. Fuel Processing Technology. 2008;89(6):574–581.
11. Hamid Tajizadegan, Azam Heidary, Omid Torabi, Mohammad-Hosein Golabgir, Amin Jamshidi. Synthesis and characterization of ZnCr2O4 nanospinel prepared via homogeneous precipitation using urea hydrolysis. International Journal of Applied Ceramic Technology. 2016;13(2):289–294.
12. Levy S, Diella D, Pavese V, Dapiaggi A. P-V equation of state, thermal expansion, and P- T stabillity of synthetic ($ZnCr_2O_4$ spinel). American Mineral. 2005;90:1157–1162.
13. Marinkovic ZV, Mancic L, Vulic P, Milosevic O. Micro structural characterization of mechanically activated ZnO–Cr2O3 system. Journal of European Ceramic Society. 2005;25:2081–2084.
14. Niu X, Du W, Du W. Preparation and gas sensing properties of ZnM_2O_4 (M = Fe, Co, Cr). Sensor Actuators B. 2004;99:405–409.
15. Yang M, Men Y, Li S, Chen G. Enhancement of catalytic activity over TiO2-modified Al2O3 and ZnO–Cr2O3 composite catalyst for hydrogen production via dimethyl ether steam reforming. Applied Catalysis A- General. 2012;433-434:26–34.
16. Zahra Mousavi, Faezeh Soofivand, Mahdiyeh Esmaeili-Zare, Masoud Salavati-Niasari, Samira Bagheri. $ZnCr_2O_4$ nanoparticles: Facile synthesis,

characterization and photocatalytic properties. Scientific Reports. 2016; 6:20071:1-11.
17. Zahra Mousavi, Faezeh Soofivand, Mahdiyeh Esmaeili-Zare, Masoud Salavati-Niasari, Samira Bagheri. ZnCr2O4 nanoparticles: Facile synthesis, characterization and photocatalytic properties. Scientific Reports 6. 2016;Article number: 20071.
18. Salahudeen A. Gene, Elias Saion, Abdul H. Shaari, Mazliana A. Kamarudin, Naif M. Al-Hada, Alireza Kharazmi. Structural, optical, and magnetic characterization of spinel zinc chromite nanocrystallines synthesised by thermal treatment method. Hindawi Publishing Corporation. Journal of Nanomaterials. 2014;Article ID 416765.
19. Hamid Tajizadegan, Azam Heidary, Omid Torabi, Mohammad-Hosein Golabgir, Amin Jamshidi. Synthesis and characterization of ZnCr2O4 nanospinel prepared via homogeneous precipitation using urea hydrolysis. International Journal of Applied Ceramic Technology, Int. J. Appl. Ceram. Technol. 2016;13(2):289–294.
20. Raghasudha M, Ravinder D, Veerasomaiah P. Characterization of nano-structured magnesium-chromium ferrites synthesized by citrate-gel auto-combustion method. Advanced Materials Letters. 2013;4(12):910-916.

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