Synthesis and Structural properties of pure and doped Cr_2O_3 nanoparticles synthesized by novel solvent free method

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Abstract— **Nanoparticles of chromium oxide (Cr_2O_3) are widely used in many fields serving as catalysts, wear resistance materials, and advanced colorants. We have reported the solvent free synthesis of Cr_2O_3 nanoparticles via microwave irradiation followed by calcinations at 200, 400, 600 and 800°c for 1h. A transparent conducting oxide is a wide band-gap semiconductor that has a relatively high concentration of free electrons in its conduction band. These arise either from defects in the material or from extrinsic dopants, the impurity levels of which lie near the conduction band edge. As implicit in the name, transparent conductors must be simultaneously transparent and conducting, an unusual combination.**

Keywords— **Nanoparticles, chromium oxide, microwave irradiation, calcined.**

I. INTRODUCTION

Nano materials, particularly transition metal oxides play an important role in many areas of chemistry, physics and material science. In the emerging field of nano technology, researchers have a goal to make nanostructures or nano arrays with special properties with respect to those of bulk or single particle species. Nano structured 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. 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. A transparent conducting oxide is a wide band-gap semiconductor that has a relatively high concentration of free electrons in its conduction band. These arise either from defects in the material or from extrinsic dopants, the impurity levels of which lie near the conduction band edge. As implicit in the name, transparent conductors must be simultaneously transparent and conducting, an unusual combination. Metal oxides as nano particles can exhibit unique chemical properties due to their limited size and high density of corner or edge surface sites. Among metal oxides, special attention has been made on the formation and properties of Cr_2O_3 for nano particles of Cr_2O_3 can be widely used in fields such as catalyst [1,2], coating, wear and corrosion resistance [3-7], advanced colorant [8-10], H_2 absorption material [11,12] and so on. It is significant to find an economical process which can be used to prepare them on a large scale. There have been some ways to obtain Cr_2O_3 nano particles, including microwave plasma [13,14], decomposition of chromium (III) nitrate solution, laser induced deposition, sono-chemical reaction, precipitation [15], mechano-chemical process [16,17], gas condensation [18] 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_2O_3 and the same is obtained successfully via novel solvent free microwave irradiation technique by the reaction system of $CrCl_3.6H_2O$ and NH_2-CO-NH_2. The effect of the molar ratio and the relationship between the structure of the crystals, time and temperatures of calcinations was studied [19]. The nano crystals of Cr_2O_3 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 gravimetrv analysis (TGA-DTA). The average particle size of the synthesized Cr_2O_3 nanoparticles is calculated using the Scherrer's formula and found to be of less than 60 nm. Also the effect on the structure and morphological properties of Cr_2O_3 when doped with 0.25, 0.5, 0.75 and 1 wt % of copper are studied.

II. EXPERIMENTAL

2.1. Materials and procedure

Chromium oxide nano-powder has been obtained via the reaction of $CrCl_3.6H_2O$ and urea using solvent free method. Urea was added at room temperature to $CrCl_3.6H_2O$ with different ratios 1:1, 1:2 and 1:3 respectively. The resulting mixture is mixed and placed under microwave irradiation. Change in colour of material to deep green indicates the completion of reaction. The molar ratio 1:3 is considered to be the best proportion to synthesis Cr2O3 nanoparticles [19]. To prepare the doped samples, 0.25, 0.5, 0.75 and 1 wt % Cu^{2+} are doped separately with Cr_2O_3 nano particles. 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_2O_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 for pure and Cu doped Cr_2O_3 nano particles on a (SEIFERT) PTS 3003 with CuKα radiation (λ=1.5406Å), operating at 40 kV and 10 mA. The diffraction data were recorded for 2θ 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 of pure and Cu doped were characterized by powder XRD analysis on a (SEIFERT) PTS 3003 with CuKα radiation (λ=1.5406Å) to discuss the variation of structural morphology. The results are discussed herein.

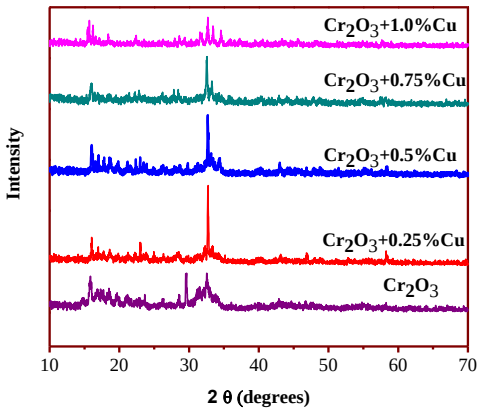


Fig 1. Comparison of XRD spectra of pure and different concentration of Cu^{2+} doped Cr_2O_3

Fig. 1 depicts the PXRD pattern observed for the pure Cr_2O_3 and copper doped Cr_2O_3 at various proportion. From the XRD patterns, it is clear that the material possesses a perfectly nano ordered lump of particles for Cr_2O_3 and Cu^{2+} doped Cr_2O_3 with differently employed dopant concentrations (0.25, 0.5, 0.75 and 1.0 wt %). The broadening of the peaks indicates the prepared samples are nano crystalline nature. The diffraction peaks (1 0 4), (1 1 3), (0 2 4), (3 0 0) and (1 1 9) indicate that the produced pure and doped Cr_2O_3 have rhombohedral structure (JCPDS card No. 01-1294). No other peaks are observed, suggesting that only single-phase Cr_2O_3 has formed. Also, from the recorded spectra, one can understand that the degree of crystallinity improves with the increasing concentration of dopant in the host Cr_2O_3. More interestingly, when Cu^{2+} is added into the pure Cr_2O_3, no diffraction peaks correspond to CuO has been observed in the XRD pattern. However the broadening of the peak is slightly increased/decreased as well as the peak intensity is also increased/decreased. Thus the lattice parameters and volume of the unit cell are slightly changed. Also the diffraction peaks gradually shifts to lower diffraction with the increase of Cu^{2+} concentration in Cr_2O_3 lattices. The continuous peak-shift may rule out the phase separation or separated nucleation of CuO and other byproducts of Cu. The peak broadening and shifting clearly indicates that the addition of dopant may replace the Cr^{3+} site or enter into the interstitial position which reveals that Cu^{2+} is incorporated with the host matrix.

The crystallite size (D) calculation for all the prepared samples (pure and doped Cr_2O_3) were performed using Scherrer's method. The crystallite sizes are found to increase with the increase of dopant concentration in the host Cr_2O_3. Due the incorporation of Cu^{2+} in the host Cr_2O_3 lattices, the diffraction peaks become narrower due to an expansion in the grain size [20]. The highest value of crystallite size calculated for Cr_2O_3:Cu^{2+} (1.0 wt %) was found to be 62.43 nm. It is also noted that the intensity of the diffraction peaks decreases for higher concentration of doping. This can be attributed to doping induced structural disorder in the parent Cr_2O_3 lattices [21]. This happens in the formation of Cr_2O_3: Cu^{2+}, because when Cu^{2+} occupies the Cr^{3+} sites in the lattice , the lattice would undergo expansion due to higher ionic radii of Cu^{2+} (0.69 Å).

Sample	Doping Concentration Weight %	Scherrer method (nm)
Cr_2O_3	-	31.96
Cr_2O_3 : Cu^{2+}	0.25	35.24
	0.5	39.13
	0.75	45.52
	1	62.43

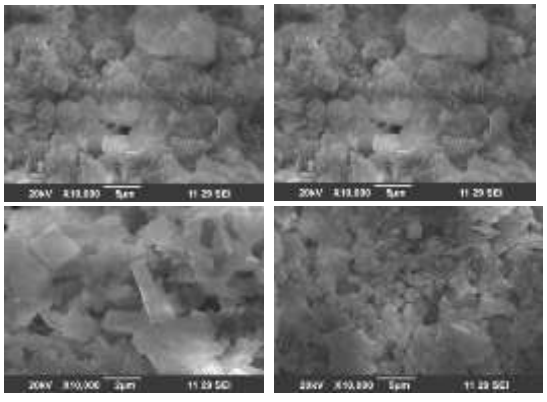


Fig 2. Sem image of Cr_2O_3

The SEM images of pure and doped Cr_2O_3 show the larger sizes and different shapes observed and may be due to the agglomeration of the nano particles during the reaction.

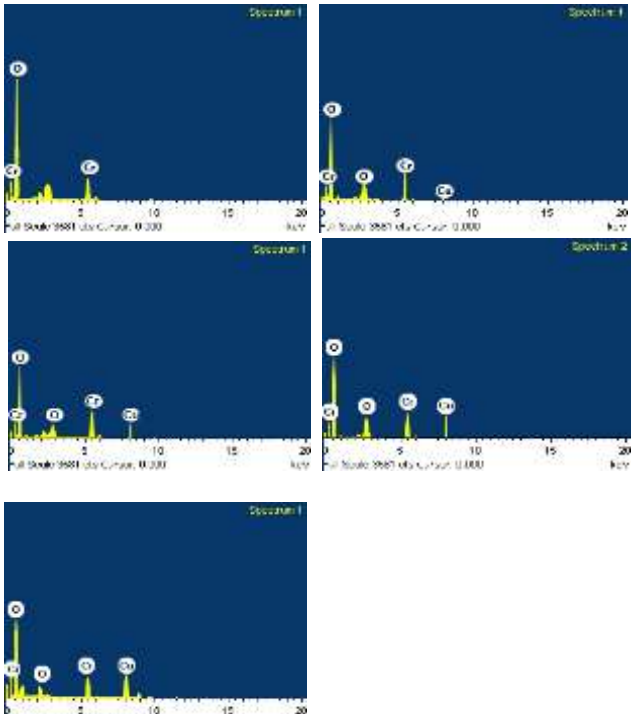
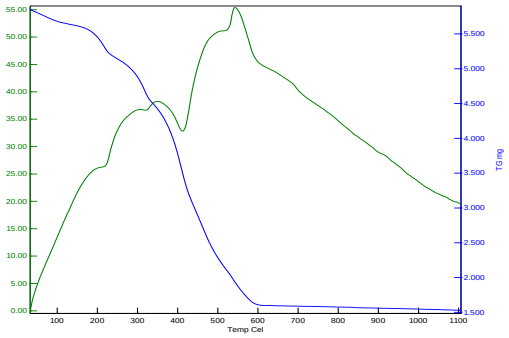


Fig 4. EDAX spectra of Cr_2O_3

Composition

The investigation of the atomic percentage and stoichiometry level, the chemical composition of the samples is done by using the energy dispersive X-ray diffractograms (EDAX patterns). The EDAX spectra of pure Cr_2O_3, Cr_2O_3 doped with different concentration of Cu^{2+} reveals that Cu^{2+} have replaced Cr^{3+} with the chosen composition (0.25, 0.5, 0.75 and 1.0 wt %). The atomic percentage of Cr decreases with increases of dopant concentration.

To identify the decomposition temperature of chromium oxide, the thermo gravimetric analysis was conducted on chromium oxide (Cr_2O_3) nano powder under flowing nitrogen. The differential thermal and thermo gravimetric curves obtained for the crystalline Cr_2O_3 nano particles are shown in Figure 2. 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. In addition, the TGA pattern shows the decomposition of the sample started at about 230^0C with a weight loss of 10.8% which may correspond to the loss of half the molecule of oxygen. Also from Figure 2, it is clear that at 330^0C a weight loss of 22% is seen which may correspond to the loss of one molecule of oxygen. Further proceeding, at about 600^0C, a weight loss of 72% is seen which may correspond to the final decomposition of 2 Cr atoms.



Thus the present study indicates that the Cr_2O_3 nano particles are stable up to 230^0C and could be used in fabricating devices which works under a temperature of 230^0C.

IV. CONCLUSIONS

A new novel method of green synthesis has been introduced to meet the demands of industrialization in the synthesis of Cr_2O_3. N type transparent conducting oxide nano particles of Cr_2O_3 were obtained successfully via novel solvent free microwave irradiation technique by the reaction system of $CrCl_3.6H_2O$ and NH_2-CO-NH_2. The novel, cost effective and simple method discussed by us provides particle size of 20 – 66 nm. The structural properties of pure and Cu^{2+} doped 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 Cr_2O_3 nanoparticles which leads to fine quantum confinement with the increase in annealing temperature. The SEM, EDAX and TGA-DTA analysis of the samples are also performed.

REFERENCES

[1] B.M.Abu Zied, "Structural and catalytic activity studies of silver/chromia catalyst", Applied Catalysis A, vol.198, no.1-2, pp, 139-153,2000.

[2] Y.F. Zhang, Z.S. Lou, Q.W. Chen, A solvothermal-reduction approach to Cr_2O_3 crystalline nanotubes synthesis, Chinese Journal of Inorganic Chemistry 20 (2004) 971–974

[3] Pang, X. Gao, K. Luo, F. Emirov, Y. Levin, A. A. and Volinsky, A.A. Investigation of micro structure and mechanical properties of multi-layer Cr/ Cr_2O_3 coatings. Thin Solid Films **517**: 1922–1927(2009).

[4] X. Hou, K.L. Choy, Synthesis of Cr2O3-based nanocomposite coatingswith incorporation of inorganic fullerene-like nanoparticles, Thin Solid Films 51 (2008) 8620–8624.

[5] M. Srivastava, J.N. Balaraju, B. Ravishankar, K.S. Rajam, Improvement in the properties of nickel by nano- Cr_2O_3 incorporation, Surface and Coating Technology 205 (2010) 66–75.

[6] Hou, X. and Choy, K.-L. Synthesis of Cr_2O_3-based nanocomposite coatings within corporation of inorganic fullerene-like nanoparticles. Thin Solid Films **516:** 8620–8624 (2008).

[7] H. Liu, J. Tao, J. Xu, Z. Chen, Q. Gao, Corrosion and tribological behaviors of chromium oxide coatings prepared by the glow-discharge plasma technique, Surface and Coating Technology 204 (2009) 28–36.

[8] T. Brock, M. Groteklaes, P. Mischke, European Coating Handbook, Vincentz Verla, Hanover, 2000

[9] Kim, D.-W. Shin, S.-I. Lee,, J.-D. and Oh, S.-G.Preparation of chromia nanoparticles by precipitation–gelation reaction. Mater. Lett. **58:** 1894-1898 (2004).

[10] Li, P. Xu, H.-B. Zhang, Y. Li, Z.-H. Zheng, S.-L. and Bai, Y.-L. The effects of Al and Ba on the colour performance of chromic oxide green pigment. Dyes and Pigments **80:** 287-291 (2009).

[11] R.Vijay,R. Sundaresan,M.P.Maiya, S. SrinivasaMurthy,Hydrogen storage properties of Mg– Cr_2O_3 nanocomposites: the role of catalyst distribution and grain size, Journal of Alloys and Compounds 424 (2006) 289–293.

[12] A. Patah, A. Takasaki, A.S. Szmyd, Influence ofmultiple oxide (Cr_2O_3/Nb2O5) addition on the sorption kinetics of MgH2, International Journal of Hydrogen Energy 34 (2009) 3032–3037

[13] W.S. Zhang, E. Bru¨ ck, Z.D. Zhang, O. Tegus, W.F. Li, P.Z. Si, D.Y. Geng, K.H.J. Buschow, structure and magnetic properties of Cr nanoparticles and Cr_2O_3 nanoparticles Physica B 358 (2005) 332–338

[14] Yin-Yu Chang , Shun-Jan Yang, Weite Wu, Plasma analyses and structural properties of Cr-N-C-O coatings synthesized by a cathodic arc evaporation process.

[15] Nipin Kohli, Onkar Singh , Kanika Anand, Ravi Chand Singh, Effect of reaction temperature on crystallite size and sensing response of chromium oxide nanoparticles. Materials Research Bulletin 47 (2012) 2072–2076

[16] T. Tsuzuki and P.G.McCormick, Synthesis of Cr_2O_3 nanoparticles by mechanochemical method Acta mater. 48 (2000) 2795±2801

[17] Partha Hajra a, PradipBrahma b, SauravDutta c, SourishBanerjee d, DipankarChakravorty, Enhancement of magnetic anisotropy in mechanically attrited Cr_2O_3 nanoparticles Journal of Magnetism and Magnetic Materials 324 (2012) 1425–1430

[18] Balchandran, U. Siegel, R.W. Liao Y. X. and Askew, T. R. Synthesis, sintering and magnetic properties of nanophase Cr_2O_3. Nanostruct. Mater. **5:** 505-512 (1995).

[19] Meenambika.R et al, "Structural and MorphologicalProperties of Cr_2O_3 Nanoparticles Synthesized By Novel Solvent Free Method **"** Int Journal of Engineering research and applications vol.4.Issue 2, February 2014, pp 20-23

[20] Jiebo Chen, Shen Lin, Guiyang Yan, Liuyi Yang andXinqin Hen, "Preparation and its Photocatalysis of Cd1−xZnxS Nano-Sized Solid Solution with PAMAM as a Template", *Catalysis Communications*, **9** (2008) 65-69

[21]. Choi J. W., Bhupathiraju A., Hasan M. A. and LannonJ. M., "Stoichiometry, Morphology and Structure of CdS Layers Grown on InP(1 0 0) from Atomic Sulfur Beam Generated from H2S gas and Thermally Evaporated Cd Using Molecular Beam Epitaxy", *J. Cryst. Growth*, **255** (2004) 1-7

