Effect of Concentration of Ni^{2+} on the Physio Chemical Properties of Cr_2O_3 Nano Particles

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Abstract

Pure and Ni^{2+} -doped Cr_2O_3 nanoparticles have been synthesized by solvothermal technique. The synthesized nanoparticles have been characterized using x-ray diffraction (XRD), ultravioletvisible spectroscopy (UV-Visible), Energy dispersive spectroscopy (EDS), and scanning electron microscopy (SEM) at room temperature. Electrical measurements were done on the pelletized samples for various temperature ranging from 30-150°C. The results are discussed herein.

1. Introduction

During the past decade, considerable progress in the synthesis of nanoparticles has been achieved. Nanomaterials, particularly transition metal oxides play an important

role in many areas of chemistry, physics and material science. Metal oxides have wide band gap because of significant contribution of ionic character to the chemical bonds between the metallic cations and oxide ions. In general metal oxides are not electrically conducting. However, current interest in material science is in unraveling the fundamental aspects of transparent conducting oxides (TCO) and their applications as semiconducting and conducting transparent thin films. 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. The physics behind TCO materials as to why they possess both high conductivity and high transparency is important in attempting to improve our understanding of them and to develop new TCO materials. To date; this combination has only been usefully realized in a limited class of metal oxides, all of which yield n-type conductors.

By comparing a variety of known materials we can establish some new transparent conductors, possibly including p-type transparent conductors and non-oxide transparent conductors.

In the emerging field of nano technology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species. Metal oxides as nanoparticles can exhibit unique chemical properties due to their limited size and high density of surface atoms [1,2]. Among metal oxides, special attention has been made on the formation and properties of Cr_2O_3 . For nanoparticles of Cr_2O_3 , though toxic [3-7] it can be widely used in fields such as catalyst [8,9], coating, wear and corrosion resistance [10,14], advanced colorant [15-17], H_2 absorption material [18,19] 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 nanoparticles, including microwave plasma [20,21], decomposition of chromium (III) nitrate solution, laser-induced deposition, sonochemical reaction, precipitation [22], mechanochemical process [23,24] gas condensation [25] 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. In this research, n-type transparent conducting oxide nanoparticles of Cr_2O_3 were obtained successfully via microwave irradiated solvothermal technique. And the effect of Ni^{2+} on the properties of Cr_2O_3 for different concentrations were investigated.

1.1 Synthesis of pure and Ni²⁺ doped Chromium oxide nanoparticles

The chemicals used in the present work were of analytical grade obtained from Sigma Aldrich, and has been used as received without any further purification treatment. In this method Cr₂O₃ nanoparticles were synthesized using CrCl₃.6H₂O as the chromium source with urea (NH₂-Co-NH₂) in molar ratio of 1:3 were mixed and dissolved in 200 ml ethylene glycol and kept in a domestic microwave oven. Then the mixture is placed under microwave irradiation for about 35 to 40 minutes. The amount of substance was calculated as follows

$$\text{Required substance} = \frac{M \times X \times V}{1000} \quad (\text{in gram units}),$$

where M is the molecular weight of the substance,
X is the concentration in molar units, and
V is the volume of solution (in Ethylene glycol).

Microwave irradiation was carried out with power 40% (About 40%: it means that if microwave works in a 60 second regime, it works 24s, and does not work 36s. This is some kind of pulse regime, but the total power is still 100 %) until the solvent gets evaporated. The colloidal precipitate obtained were cooled to room temperature and the precipitate was collected and washed with distilled water for several times. Approximately 10 liters of distilled water was used for washing purpose. Later the above purified colloidal particles were centrifuged for further purification with 7000rpm. As collected particles were washed with acetone to remove organic impurities if present any. Then 98% pure Cr₂O₃ particles were collected and kept in hot air oven at 70°C for about 48hrs. For the impurity added Cr₂O₃ nano particles, Nickel chloride have been added with the above sol in different concentrations namely 2.5, 5 and 7.5 mole %. The dried samples were collected as a yield for coating thin films.

2. Methods

X-ray powder diffraction patterns were obtained using an automated P-analytical X-ray powder diffractometer with monochromated CuK_α radiation (λ=1.5405 Å). The crystallite size analysis were made using Scherrer [18] method. Microstructural analysis has been performed using SEM Zeiss-SUPRA 40 by secondary electron imaging mode. Chemical composition and the presence of dopant in Cr₂O₃ lattice was analysed by recording EDAX spectra using Jeol make JSM 5600 LV Model attached with Energy Dispersive Spectrometer of EDAX inc . Optical characteristics of the as

prepared samples were explained by recording UV-visible absorption spectra in the range of 180-900nm. The resultant powder materials prepared in the present study were compacted into disc shaped pellets of dimensions 13 mm in diameter and 1.5 mm (± 0.025 mm) in thickness with 4 ton hydraulic pressure. The dimensions of the pellets were measured using a travelling microscope (L.C. = 0.01 mm). The pelletized samples were annealed for two hours at ~ 150 °C to achieve densification. After the sintering process, both surfaces of the sample were coated with silver paste to obtain a good conductive surface layer. The capacitance (C) and dielectric loss factor ($\tan\delta$) measurements were carried out to an accuracy of ± 1 % with Agilent 4284A LCR meter in the temperature range of 40 – 130 °C. The observations were made while cooling the sample. Temperature was controlled to an accuracy level of ± 0.5 °C. The observations were made using the conventional two-probe technique [17]. Air capacitance (C_{air}) was also measured. The dielectric constant (ϵ_r) of the crystal was calculated using the relation,

$$\epsilon_r = \frac{C}{C_{\text{air}}}. \quad (1)$$

The AC electrical conductivity (σ_{ac}) was calculated using the relation

$$\sigma_{\text{ac}} = \epsilon_0 \epsilon_r \omega \tan\delta, \quad (2)$$

where ϵ_0 is the permittivity of free space (8.854×10^{-12} F/m) and ω is the angular frequency ($\omega = 2\pi f$; $f = 1$ kHz in the present study).

3. Results and Discussion

3.1 PXRD Analysis

Figure 2 shows the room temperature X-ray diffraction pattern of the pure and Ni^{2+} doped (2.5, 5 and 7.5 mole %.) Cr_2O_3 nanoparticles. Inspection of the results revealed that pure Cr_2O_3 thus formed is of rhombohedral phase (JCPDS no. 38-1479 with $a=4.95876$ Å, $c=13.594$ Å and space group $R\bar{3}c$). No characteristic peaks of nickel impurity (such as NiS, NiO) were detected, at least within the resolution limit of the diffractometer. In all of the XRD patterns, the broadening of the diffraction peaks of the nanoparticles is obvious, which is characteristic of nanosized materials. The average crystalline sizes of the samples were estimated from the half-width of diffraction peaks using the Debye–Scherrer formula. The observed structural data and crystallite sizes of the samples from the XRD are summarized in Table 1. Upon the doping as shown in fig.2, the diffraction peaks sharpness improved with respect to the dopant concentration and the full width half maximum [FWHM] values decreased with increasing dopant concentration.

Figure 1: Powder XRD patterns of (a) Cr_2O_3 (b) Cr_2O_3 :2.5 % Ni^{2+} (c) Cr_2O_3 :5 % Ni^{2+} and (d) Cr_2O_3 :7.5 % Ni^{2+} nanoparticles

Table 1: Summary of structural data, crystallite size and obtained yield percentage of pure and Ni^{2+} doped Cr_2O_3 nanoparticles

Sample	Lattice parameters			Reaction Time (min)	Yield %	Crystallite size (nm)
	a=b (Å)	c (Å)	Volume (Å ³)			
Pure Cr_2O_3	4.951	13.598	288.75	24	17.52	28.52
Cr_2O_3 with 2.5% Ni^{2+}	4.954	13.62	290.33	26	19.56	27.21
Cr_2O_3 with 5% Ni^{2+}	4.962	13.71	290.33	29	21.42	25.63
Cr_2O_3 with 7.5% Ni^{2+}	4.968	13.75	289.49	32	24.63	22.32

3.2 SEM –EDAX Analysis

Incorporation of dopant in Cr_2O_3 lattice was confirmed by EDAX spectra. Figure 3 shows the EDAX spectra of pure and Ni^{2+} doped Cr_2O_3 nano particles. In order to understand whether doping treatment indeed play a role in the microstructure, we have carried out SEM study of the doped and undoped Cr_2O_3 nanoparticles. The comparison is shown in Figure 4.

Figure 2: EDAX spectra of (a) Cr_2O_3 (b) $\text{Cr}_2\text{O}_3 : 2.5 \% \text{Ni}^{2+}$ (c) $\text{Cr}_2\text{O}_3 : 5 \% \text{Ni}^{2+}$ and (d) $\text{Cr}_2\text{O}_3 : 7.5 \% \text{Ni}^{2+}$ nanoparticles

Figure 3: SEM images of (a) Cr_2O_3 (b) $\text{Cr}_2\text{O}_3 : 2.5 \% \text{Ni}^{2+}$ (c) $\text{Cr}_2\text{O}_3 : 5 \% \text{Ni}^{2+}$ and (d) $\text{Cr}_2\text{O}_3 : 7.5 \% \text{Ni}^{2+}$ nanoparticles

3.3 UV-VIS Analysis

Optical absorption measurements were done at room temperature on the pelletized samples using a Shimadzu UV spectrophotometer with a medium scan speed sampling interval 1 nm in the wavelength range 200-2000 nm. Figure 4 shows the optical absorption spectrum of the pure, Ni^{2+} (different mole %) doped Cr_2O_3 nano-

particles. The corresponding energy vs $(\alpha h\nu)^2$ plot is given in Figure 4b. The observed optical bandgap energy values are 3.33, 3.49, 3.62 and 3.68 eV for Pure Cr_2O_3 , 2.5, 5 and 7.5 mole % Ni^{2+} doped Cr_2O_3 nano particles respectively. The bandgap observed for the doped Cr_2O_3 nanocrystals are higher than the pure Cr_2O_3 . It is known that semiconductor nanocrystals with crystallite size significantly smaller than the exciton Bohr radius show size-dependent optical properties due to the strong quantum confinement effect for the charge carriers. A weak quantum confinement effect occurs when the crystallite size is larger than the Bohr radius [26]. It is known that the typical exciton Bohr radius for Cr_2O_3 is 3 nm [27].

Figure 4: UV optical spectra and Tau plot of pure and doped Cr_2O_3 nano particles

3.4 Electrical Analysis

It is also known that the electrical behavior of nanostructured materials is strongly influenced by geometrical factors [22]. Figure 5 shows the temperature dependence of electrical parameters such as ϵ_r , $\tan \delta$ and σ_{ac} observed in the present study for the temperature range of 40 to 130 °C at a constant frequency (1 kHz). It can be seen that all the three electrical parameters increase with the increase in temperature also the electrical parameters increases with increasing impurity concentration from 5 to 7.5 mole % considered in the present study. The electrical resistivity of nanocrystalline materials is higher than that of both conventional coarse grained polycrystalline materials and alloys. The magnitude of electrical resistivity and hence the conductivity of nanomaterials (or quantum dots) can be changed by altering the size of the electrically conducting component. In the present case, the observed σ_{ac} values are very small. When the crystallite size (the obtained crystallite size of all the synthesized samples are less than 20 nm) is smaller than the electron mean free path,

grain boundary scattering dominates and hence the electrical resistivity is high as compared with the corresponding bulk counterpart.

Figure 5: Variation of Electrical parameter (ϵ_r , $\tan \delta$ and σ_{ac}) for pure and doped Cr_2O_3 at 1kHz.

4. Conclusion

Pure and different concentrated Ni^{2+} doped Cr_2O_3 nanoparticles were synthesized by simple cost effective microwave technique. Increase in concentration of dopant, decreases the crystallite size of the pure Cr_2O_3 which leads to strong quantum confinement. As the particle size decreases, the increasing number of surface and interface atoms generates stress/strain and concomitant structural perturbations. A decrease in the average size of an oxide particle do in fact change the magnitude of the band gap with strong influence in the conductivity and chemical reactivity of Cr_2O_3 .

References

- [1] Fernandez-Garcia.M, Martinez-Arias.A, Hanson.J.C and Rodriguez. J.A. "Nanostructured oxides in chemistry: characterization and properties", Chem. Rev, **104**: 4063-4104(2004).
- [2] Tsoncheva.T, Roggenbuck. J , Paneva.D, Dimitrov.M, Mitov.I. and Froba.M. "Nanosized Iron and Chromium Oxides supported on mesoporous CeO₂ and SBA-15 silica", Physiochemical and catalytic study, Appl.Surf. Sci. **257**,523-530(2010)
- [3] Khatereh khorsandi, Azra Rabbani-Chadegani. "Studies on the genotoxic effect of chromium oxide, Interaction with deoxyribonucleic acid in solution", Genetic Toxicology and Environmental Mutagenesis, **750**, 105-110(2013)
- [4] Amany El-Sikaily, Ahmed El Nemr, Azza Khaled, Ola Abdelwehab. "Removal of toxic chromium from wastewater using green alga *Ulva lactuca* and its activated carbon", Hazardous Materials, **148**, 216-228(2007)
- [5] N.K. Chandra Babu, K. Asma, A. Raghupathi, R. Venba, R. Ramesh, S. Sadulla. "Screening of leather auxiliaries for their role in toxic hexavalent chromium formation in leather posing potential health hazards to the users", Cleaner Production, **13**, 1189-1195(2005)
- [6] Arun K. Shanker, Carlos Cervantes, Herminia Loza-Tavera, S. Avudainayagam. "Chromium toxicity in plants", Environment International,**31**,739-753(2005).
- [7] Ahmad B. Albadarin, Ala'a H. Al-Muhtaseb, Nasir A. Al-Iqtah, Gavin M. Walker, Stephen J. Allen, Mohammad N.M. Ahmad. "Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts", Chemical Engineering, **169**, 20-30(2011)
- [8] B.M.Abu Zied, "Structural and catalytic activity studies of silver/chromia catalyst", Applied Catalysis A, **198**, no.1-2, 139-153(2000).
- [9] Y.F. Zhang, Z.S. Lou, Q.W. Chen, "A solvothermal-reduction approach to Cr₂O₃ crystalline nanotubes synthesis", Chinese Journal of Inorganic Chemistry, **20**, 971-974 (2004)
- [10] 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/ Cr₂O₃ coatings", Thin Solid Films, **517**, 1922-1927(2009).
- [11] X. Hou, K.L. Choy, "Synthesis of Cr₂O₃-based nanocomposite coatings with incorporation of inorganic fullerene-like nanoparticles", Thin Solid Films, **51**, 8620-8624(2008).
- [12] M. Srivastava, J.N. Balaraju, B. Ravishankar, K.S. Rajam, "Improvement in the properties of nickel by nano- Cr₂O₃ incorporation", Surface and Coating Technology, **205**, 66-75(2010).

- [13] Hou, X. and Choy, K.-L. "Synthesis of Cr_2O_3 -based nanocomposite coatings within incorporation of inorganic fullerene-like nanoparticles", *Thin Solid Films*, **516**, 8620–8624 (2008).
- [14] 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**, 28–36(2009).
- [15] T. Brock, M. Groteklaes, P. Mischke, *European Coating Handbook*, Vincentz Verla, Hanover, (2000).
- [16] 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).
- [17] 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).
- [18] R. Vijay, R. Sundaresan, M.P. Maiya, S. Srinivasa Murthy. "Hydrogen storage properties of Mg– Cr_2O_3 nanocomposites: the role of catalyst distribution and grain size", *Journal of Alloys and Compounds*, **424**, 289–293(2006).
- [19] A. Patah, A. Takasaki, A.S. Szmyd, "Influence of multiple oxide ($\text{Cr}_2\text{O}_3/\text{Nb}_2\text{O}_5$) addition on the sorption kinetics of MgH_2 ", *International Journal of Hydrogen Energy*, **34**, 3032–3037(2009).
- [20] W.S. Zhang, E. Bruck, 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**, 332–338(2005).
- [21] 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".
- [22] 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**, 2072–2076(2012).
- [23] T. Tsuzuki and P.G. McCormick. "Synthesis of Cr_2O_3 nanoparticles by mechanochemical method", *Acta mater.*, **48**, 2795–2801(2000).
- [24] Partha Hajra, Pradip Brahma, Saurav Dutta, Sourish Banerjee, Dipankar Chakravorty. "Enhancement of magnetic anisotropy in mechanically attrited Cr_2O_3 nanoparticles", *Journal of Magnetism and Magnetic Materials*, **324**, 1425–1430(2012).
- [25] 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).

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