PREPARATION AND CHARACTERIZATION OF FE_2O_3 MODIFIED NANOCRYSTALLINE CR_2O_3 BASED THICK FILMS

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Abstract

Pure and Iron (Fe) doped chromium (III) oxide (Cr_2O_3) nanoparticles have been prepared by co-precipitation method. Structural behavior of Cr_2O_3 nanoparticles was examined by X-ray diffraction (XRD) and the average crystallite size of the synthesized Cr_2O_3 nanoparticles was measured from XRD patterns using Scherrer equation and was found to be ~23 nm. Almost uniform and spherical-like morphologies and compositional elements of the synthesized nanoparticles were observed by the field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) spectroscopy, respectively. Thick films of pure Cr_2O_3 were prepared by screen-printing technique. The surfaces of these films were modified by dipping them into a 0.01M aqueous solution of ferric chloride ($FeCl_3$) for different intervals of time, followed by firing at 550 ^{0}C for 30 min. The firing resulted in the oxidation of the $FeCl_3$ additive into. Fe_2O_3 i.e Fe_2O_3 modified Cr_2O_3 thick films.

Keywords: Nanocrystalline; Chromium Oxide; Thick films; Additives

1. Introduction

Transition metal oxides have attracted a great deal of attention in recent years, due to to their unique physical, chemical, optical, electrical and magnetic properties [1–5]. Among various transition metal oxides, Cr_2O_3 is one of the widely investigated material because of its wide band gap (~3.3 eV) [6]. Cr_2O_3 is an intrinsic semiconductor nature at high temperature (>1000ºC), whereas extrinsic p-type semiconductor nature at lower temperatures [7, 8]. This kind of p-type wide band gap oxide semiconductors may be a good candidate for numerous applications. The applications of Cr_2O_3 material depends not only on their composition and an addition of suitable dopants but also on their structure, phase, shape, size and synthesizing techniques. As a result, the synthesis of nanomaterials with large surface area to volume (lesser particle size) and high chemical activities has been the subject of active research.

Different preparation techniques for synthesis of Cr_2O_3 nanoparticles have been reported in the literature. For most of the techniques, highly explosive reactants, more complex processes, environmentally sensitive, more expensive reaction apparatus and higher calcination temperature is required. Moreover, most of methods produced a nonhomogenous particle size distribution, highly agglomerated and low yields. Among them, co-precipitation is considered as a cost effective and a less time consuming route. This technique can be used for the production of high purity nanocrystalline Cr_2O_3 on large scale.

So, the aim of the present work is to prepare nanocrystalline Cr_2O_3 by co-precipitation route to investigate the effect of Fe_2O_3 modification on structural and morphological behaviour of Cr_2O_3 based thick films fabricated by screen printing technique.

2. Experimental

2.1. Synthesis of Cr_2O_3 nanostructure

In present work 25·50gm $Cu(NO_3)_3 \cdot 9H_2O$ was dissolved in 50 ml double distilled water and then kept on magnetic stirrer at 80°C for 1h, a transparent solution was formed. In this solution ammonia was added drop wise until a precipitated of pH 9 was formed. After ageing at room temperature for overnight the Chromium hydroxide was recovered by filteration, washing with double distilled water and drying at 110^0C for 24h Cr_2O_3 nanomaterial was obtained by calcinig Chromium hydroxide at 500^0C and 600^0C for 5 hours. The synthesized Cr_2O_3 nanostructure product was used for further study.

2.2. Preparation of thick films

Thick films of Cr_2O_3 nanostructure were prepared by using screen printing technique. In this process paste was formulated by mixing the synthesized Cr_2O_3 nanostructure. Powder with ethyl cellulose (a temporary binder) in mixture of three organic solvents. The ratio of inorganic to organic part was kept as 75:25 in formulating the pastes. The ready pastes were screen printed on a glass substrate in desired patterns. The films prepared were fired at 500^0C for 12h. Prepared thick films termed as pure Cr_2O_3 thick films.

2.3. Fe_2O_3 modified Cr_2O_3 thick films

Surface of pure Cr_2O_3 thick films were modified by dipping them into 0.01M aqueous solution of $FeCl_3$ (99%ARgrade, Merck) for different intervals of time (2, 3, 4 min.) Dipped thick films were dried under IR lamp for 1h. Dried thick films were fired at 500^0C for 30min. The $FeCl_3$ dispersed on the film surface was oxidised to Fe_2O_3 in firing process and sensor elements with different mass % of Fe_2O_3 on the surface of Cr_2O_3 thick films were obtained. These surface modified thick films are termed as Fe_2O_3 modified Cr_2O_3 thick films.

3. Results and discussion

3.1. X-ray diffraction studies

Fig. 1 shows X-ray diffraction (XRD) patterns of synthesized Cr_2O_3 powder samples, the observed peaks are matching well with JCPDS data of Cr_2O_3. The characteristic peaks observed in the spectrum are higher in intensity which indicates that the as-synthesized samples are of good crystalline nature. The average crystallite size (D) was estimated from the Debye–Scherrer's equation: $D = 0.9\ \lambda / \beta \cos\theta$; where λ is the wavelength of X-rays (1.54056 Å), β is the FWHM, θ is the diffraction angle at which the full width at half maximum (FWHM) measured.

The average crystallite size of the synthesized Cr_2O_3 nanoparticles was measured from XRD patterns using Scherrer equation and was found to be ~23 nm.

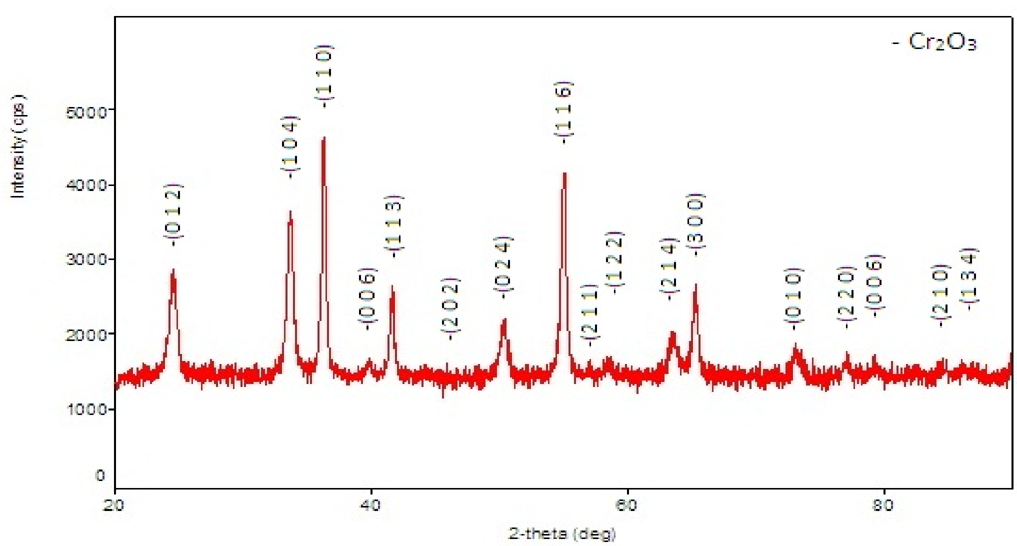
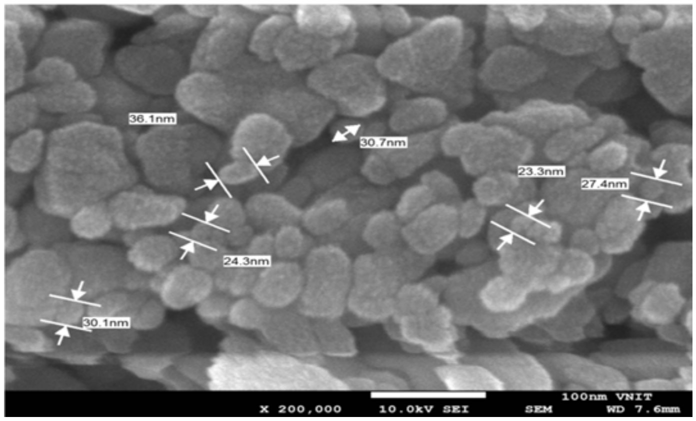


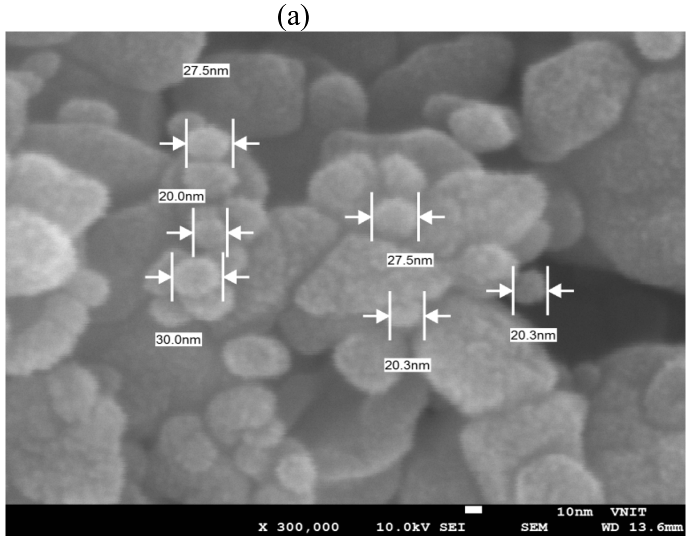
Fig. 1: X-ray diffraction pattern of Cr_2O_3 powder sample calcinated at 600 ^{0}C.

3.2. Scanning electron microscopic study

Fig. 2 (a-d) shows typical FE-SEM images of the pure and Fe_2O_3 modified Cr_2O_3 thick films prepared by screen printing technique. It can be seen from Fig. 2 (a) that the pure Cr_2O_3 nanoparticles were nearly uniform spherical shapes and very small particles in evidently dispersed without large agglomerates. Fig. 2 (b-d) depicts the microstructure of Fe_2O_3 modified film for 2 min., 3 min. and 4 min., respectively, consist of particles with smaller size and shape associated with the Cr_2O_3 grains. Moreover, it can be seen that there is decrease in the agglomerations with the increase in the content of Fe. The average grain size of the fabricated thick films is observed to be in the range of 20 nm to 28 nm.



(a)



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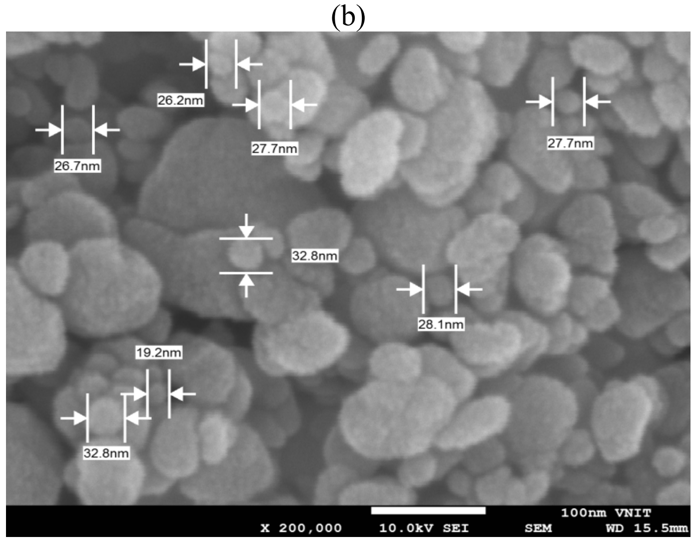

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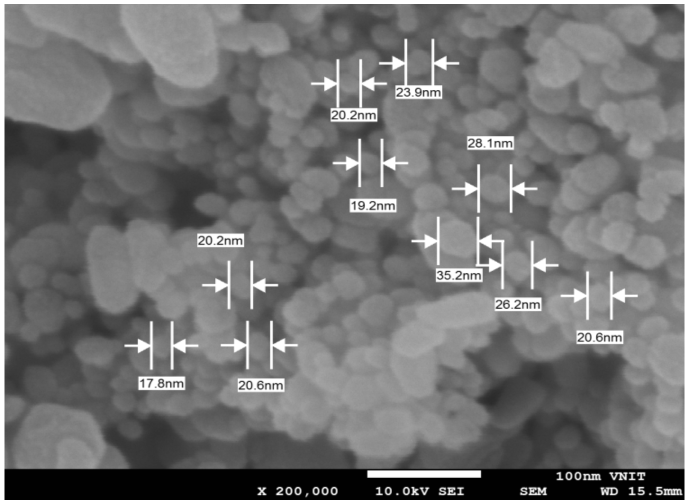

(d)

Fig. 2: FE-SEM microstructures for (a) Cr_2O_3 nanoparticles (b) Fe_2O_3 modified Cr_2O_3 thick films (2 min.) (c) Fe_2O_3 modified Cr_2O_3 thick films (3 min.) (d) Fe_2O_3 modified Cr_2O_3 thick films (4 min.).

4. Conclusions

In this paper, nanocrystalline Cr_2O_3 has been successfully prepared by co-precipitation method. The average crystallite size of as-prepared Cr_2O_3 has been estimated to be ~23 nm. The as-prepared nanoparticles are high purity, composition and produced with minimal agglomeration. The crystallite sizes calculated from XRD data show good agreement with those particle sizes obtained by FE-SEM. The morphological characterization of pure and Fe_2O_3 modified Cr_2O_3 thick films reveals that there is decrease in the agglomerations with the increase in the content of Fe.

References

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