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Cr_2O_3 Nanoparticles: Synthesis, Characterization, and Magnetic Properties

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ABSTRACT

In this paper, semi-solid precursor of chromium was prepared from the reaction of $Cr(NO_3)_3$ and oxalic acid at the presence of NaOH. Then Cr_2O_3 nanoparticles were prepared by solid-state thermal decomposition of this precursor at 500 and 600 ºC, at standard atmospheric pressure for 3 h. The as-prepared Cr_2O_3 nanoparticles were characterized by Fourier transform infrared (FT-IR), ultraviolet-visible (UV-Vis) spectroscopy, X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM). The sharp vibration bands in FT-IR spectra and high intensity peaks in XRD patterns confirmed the preparation of pure, single rhombohedral phase and crystalline Eskolaite structure of Cr_2O_3 nanoparticles. A broad absorption peak appeared at UV-Vis spectra indicates the d^3 electronic transition of Cr^{3+}. The TEM images show that the particles are similar and a little agglomerated with the average crystal size of < 100 nm. The VSM results predict that the as-prepared Cr_2O_3 nanoparticles are weak ferromagnetic and paramagnetic.

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INTRODUCTION

Cr_2O_3, as trivalent oxide, is more stable than other well-known chromium oxide such as hexavalent CrO_3 and tetravalent CrO_2 [1]. It is an antiferromagnetic material with a wide band gap (Eg ≈ 3.4 eV) taht exhibits *n*-type or *p*-type semiconductor behavior [2] and used as green colourant in the pigment industry for ceramic, coating, paints and printing [2]. It has been investigated as a Li cathode [3,4], solar absorber [5,6], catalyst [7], and hydrogen sorption [8]. It is also employed in electrohydrogenation [9], dehydrogenation [10], removal of dyes [11], biomedical application [12] and gas sensing [13]. According to the literature, single-phase synthesis and regulation of the morphology of the of Cr_2O_3 nanoparticles are difficult to perform [14]. Until now, Cr_2O_3 nanoparticles have been synthesized by various techniques such as microwave-assisted [15,16], thermal decomposition [17], hydrothermal [18,19], green chemistry [2,20,21], solvothermal [22], template-free approach [23,24] and other methods [25,26]. All of these techniques are complex, time consuming, and require expensive equipment.

The aim of this study is preparation of pure and single phase chromium oxide (Cr_2O_3) nanoparticles from low-cost starting materials, in a simple and easy method (thermal decomposition) and characterization of their structure, shape, size, optical and magnetic properties (Fig. 1).

EXPERIMENTAL

Materials and Methods

$Cr(NO_3)_2.6H_2O$, oxalic acid, and NaOH were purchased from Merck company and used without future purification. FT-IR and UV-Vis spectra were carried out using a Perkin-Elmer and Jasco spectrophotometer, respectively. The X-ray patterns were performed with a Bruker AXS diffractometer D8 ADVANCE in the range 2θ = 10º–80º. The TEM

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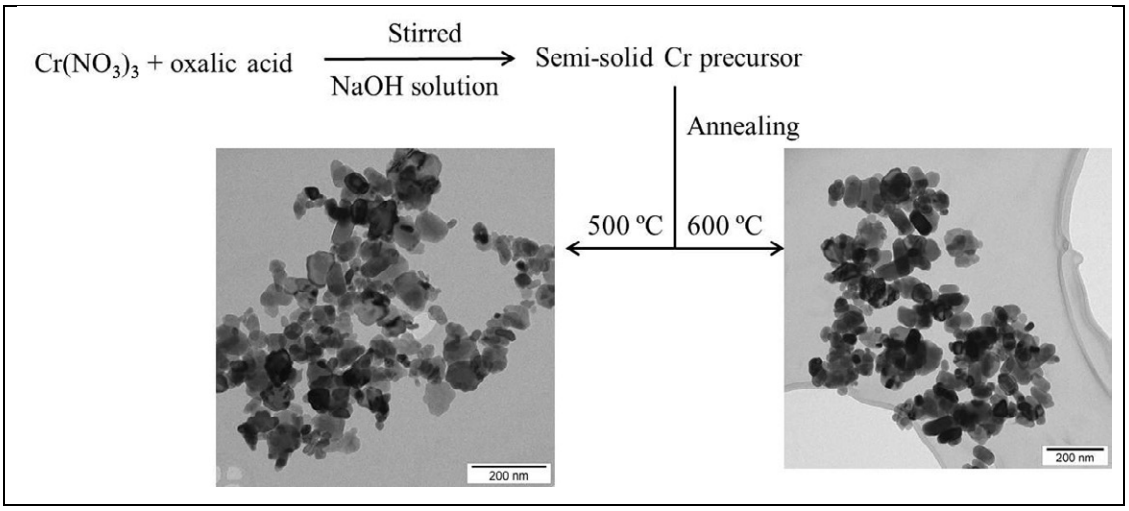

Fig. 1. Schematic illustration of the Cr_2O_3 nanoparticles preparation

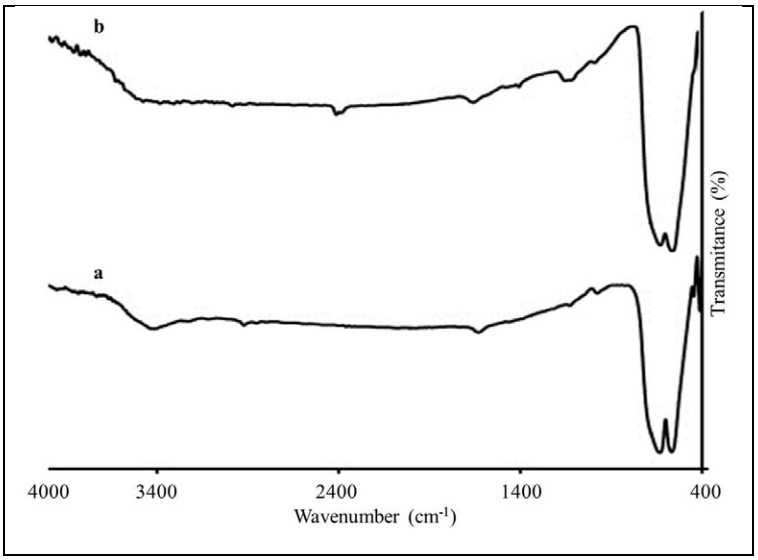

Fig. 2. FT-IR spectra of Cr_2O_3 nanoparticles prepared at a) 500 ºC and b) 600 ºC

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 $Cr(NO_3)_2.6H_2O$ (1 mmol) and oxalic acid (3 mmol) were dissolved into 15 mL of distilled water and stirred for 20 min to prepare a clear solution. To this solution, an aqueous solution of NaOH was added dropwisely until reaching pH 12, and the mixture was then heated up to 80 ºC. After cooling to r.t. the semi-solid products obtained were divided into two equal parts and heated at temperatures of 500 and 600 ºC for 3 h. The as-prepared Cr_2O_3 nanoparticles were washed with distilled water (twice) and dried at 80 ºC in a furnace for 24 h. Finally, the products were characterized by FT-IR, UV-Vis, XRD, TEM and VSM.

RESULTS AND DISCUSSION

Fig. 2 shows the FT-IR spectra of the as-prepared Cr_2O_3 nanoparticles that matches well with previous reports [14,18]. The sharp vibration bands at 627 and 562 cm^{-1} and 630 and 565 cm^{-1} of Cr_2O_3 nanoparticles prepared at 500 ºC and 600 ºC, respectively, are assigned to the Cr-O stretching

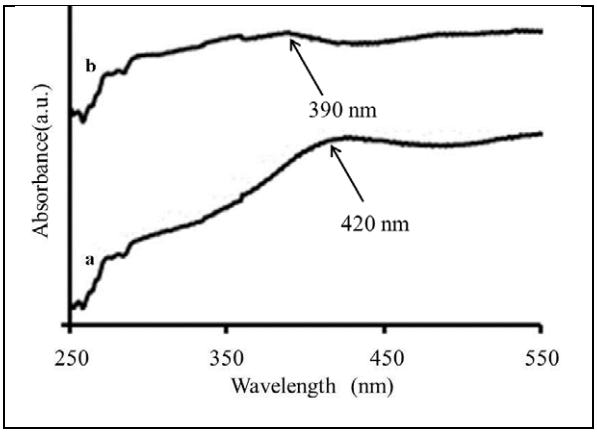

Fig. 3. UV-Vis spectra of Cr_2O_3 nanoparticles prepared at a) 500 °C and b) 600 °C

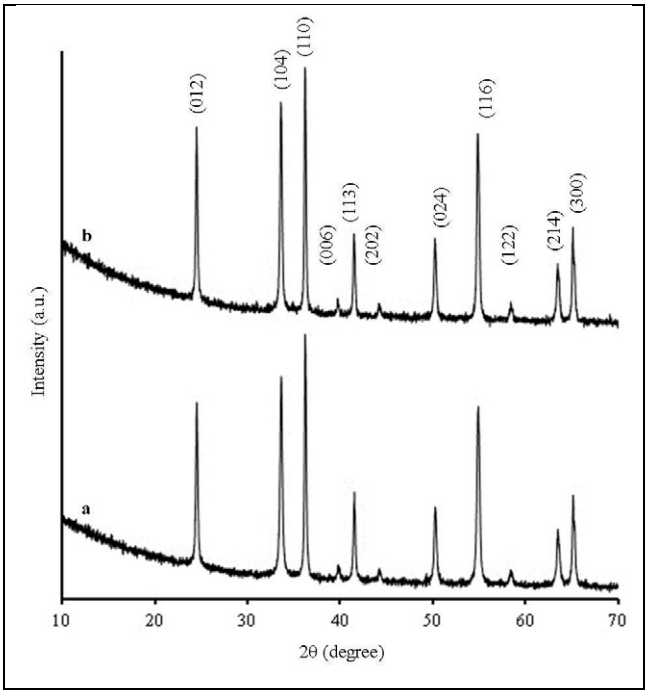

Fig. 4. XRD patterns of Cr_2O_3 nanoparticles prepared at a) 500 °C and b) 600 °C

vibrations indicating the presence of the crystalline Cr_2O_3 [14,18,24]. The appearance of a shoulder in wave numbers at about 690 cm^{-1} predicts the presence of other morphologies for the as-prepared Cr_2O_3 nanoparticles [27]. The two weak and broad bands at about 1630 cm^{-1} and 3415 cm^{-1} are due to the O-H vibration of water molecules adsorbed on the surfaces of the as-prepared Cr_2O_3 nanoparticles [14].

Fig. 3 represents the UV-Vis spectra of Cr_2O_3 nanoparticles. Broad absorption peak appeared at about 420 nm for Cr_2O_3 nanoparticles prepared at 500 °C indicates the d^3 electronic transition of Cr^{3+} [22,24], confirmed the six-coordinate geometry with octahedral symmetry around Cr^{3+} ion. While this peak is blue shift to 390 nm for Cr_2O_3 nanoparticles prepared at 600 °C. A similar peak is seen at 455 nm for the nanocubes of Cr_2O_3 reported by Roy *et al* [24] and nanoparticles of Cr_2O_3 reported by Anandan and Rajendran [22].

After calcination of chromium precursor at 500 and 600 °C, pure rhombohedral phase and crystalline Eskolaite structures of Cr_2O_3 (JCPDS card # 38-1479) were obtained [17,24]. The XRD

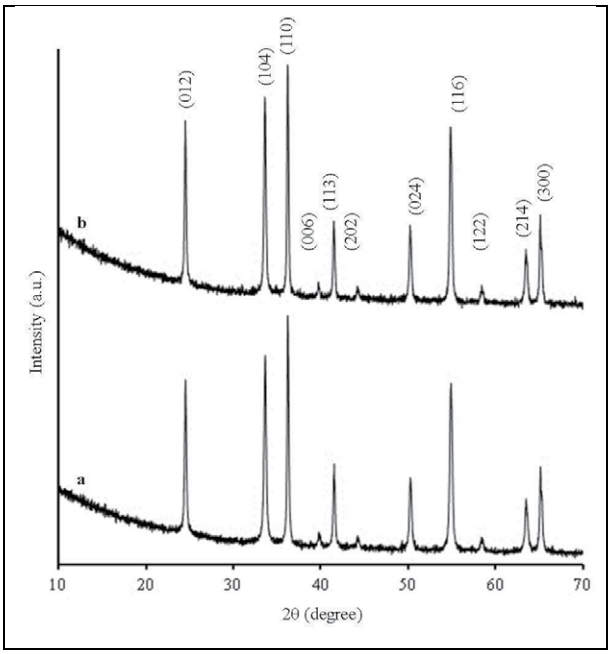

Fig. 5. TEM images of Cr_2O_3 nanoparticles prepared at a) 500 °C and b) 600 °C

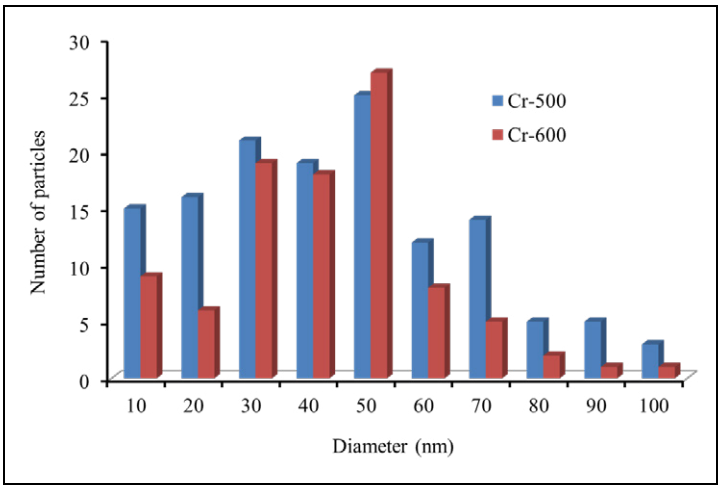

Fig. 6. Particle size distribution of Cr_2O_3 nanoparticles prepared at a) 500 °C and b) 600 °C

patterns of the Cr_2O_3 nanoparticles are presented in Fig. 4. The XRD patterns show that the all diffraction peaks are high and broad due to the pure, small size and well crystallized Cr_2O_3 nanoparticles [17,22], also no extra peaks, pertaining the impurities, were detected. The intensities of the diffraction peaks in the XRD patterns were almost equal, indicating that the temperature increasing does not change the crystalline size and crystallinity of the products. The average crystallite sizes were found to be about 50 nm, according to Debye-Scherrer's equation:

$$D = 0.9 \lambda / \beta \cos \theta$$

where λ is the X-ray wavelength, β is full width at half maximum (FWHM) in radiation and θ is the diffraction angle of the sharp peak.

Fig. 5 shows the TEM images of the synthesized Cr_2O_3 nanoparicles and confirmed the size distribution is not homogeneous; nearly rectangle and is in a range of about 10 – 100 nm. By

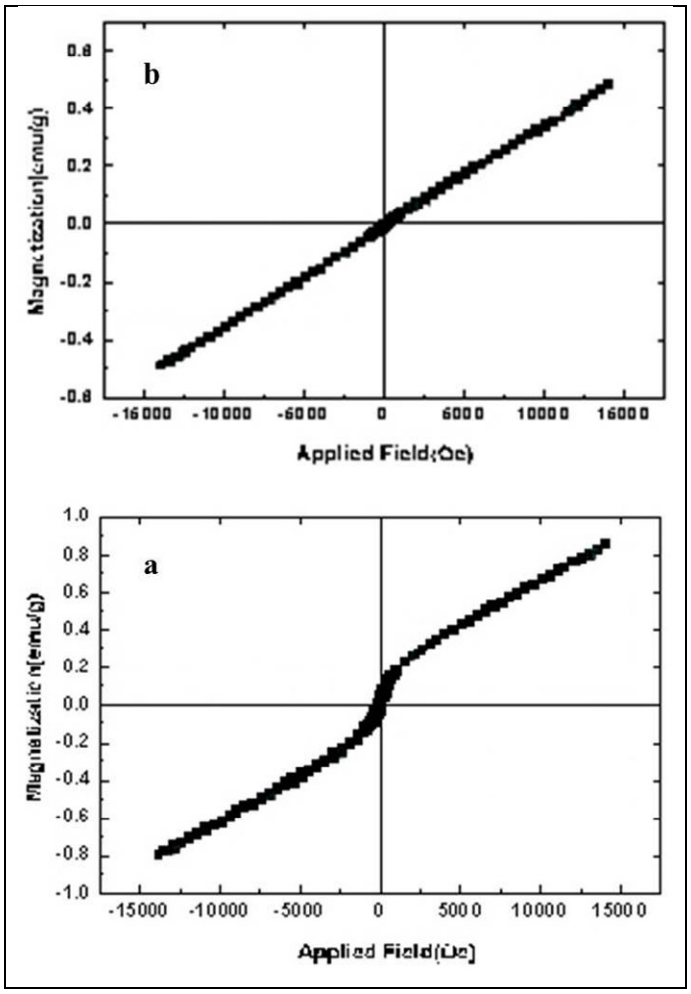

Fig. 7. VSM test of Cr_2O_3 nanoparticles prepared at a) 500 °C and b) 600 °C

increasing the temperature to 600 °C, the Cr_2O_3 nanoparticles obtained were uniform in size and shape (Fig. 5b). A similar result as reported by Su *et al*. is obtained for the spherical Cr_2O_3 nanoparticles [16]. Further research is necessary to understand the changes that occur in the surface morphology of the products [16].

The size distribution of the particles, shown in Fig 6, confirmed that the average particle sizes determined by the TEM study are in good agreement with the average particle sizes calculated by Debye-Scherrer's equation.

Fig. 7 illustrated the VSM of the synthesized Cr_2O_3 nanoparticles. The curve for Cr_2O_3 nanoparticles prepared at 500 °C is nearly linear and does not show any magnetic saturation, indicating the paramagnetic contribution [25]. While the curve is not linear for Cr_2O_3 nanoparticles prepared at 600 °C, it shows a weak ferromagnetic behavior due to the different sizes and shapes of the nanoparticles [26].

CONCLUSION

The Cr_2O_3 nanoparticles were synthesized via a fast, simple, and low cost technique of thermal decomposition and characterized by various techniques. The purity and single rhombohedral phase were confirmed by XRD and FT-IR. The average size and morphology of the products were examined using TEM and found to be the size distribution is not homogeneous and rectangle nanostructures are in a range of about 10 – 100 nm. The Cr_2O_3 nanoparticles obtained at 600 °C show the better distribution in size and shape. The magnetic properties indicated paramagnetic and weak ferromagnetic nature of the Cr_2O_3 products

prepared at 500 and 600°C, respectively.

ACKNOWLEDGMENTS

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CONFLICT OF INTEREST

The author declared to no conflict of interest.

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