Cr$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ nanoparticles are weak ferromagnetic and paramagnetic.

INTRODUCTION

Cr$_2$O$_3$, 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 $\approx$ 3.4 eV) that 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$_2$O$_3$ nanoparticles are difficult to perform [14]. Until now, Cr$_2$O$_3$ 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$_2$O$_3$) 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$_3$)$_3$.6H$_2$O, 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 20 = 10°–80°. The TEM
images were recorded on transmission electron microscope Philips with CCD camera Olympus Veleta. The magnetic properties were investigated by vibrating sample magnetometer.

**Synthesis of Cr₂O₃ nanoparticles**

A mixture of Cr(NO₃)₂·6H₂O (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 Cr₂O₃ 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 Cr₂O₃ 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 Cr₂O₃ nanoparticles prepared at 500 ºC and 600 ºC, respectively, are assigned to the Cr-O stretching.
vibrations indicating the presence of the crystalline Cr$_2$O$_3$ [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$_2$O$_3$ 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$_2$O$_3$ nanoparticles [14].

Fig. 3 represents the UV-Vis spectra of Cr$_2$O$_3$ nanoparticles. Broad absorption peak appeared at about 420 nm for Cr$_2$O$_3$ nanoparticles prepared at 500 ºC 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$_2$O$_3$ nanoparticles prepared at 600 ºC. A similar peak is seen at 455 nm for the nanocubes of Cr$_2$O$_3$ reported by Roy et al [24] and nanoparticles of Cr$_2$O$_3$ reported by Anandan and Rajendran [22].

After calcination of chromium precursor at 500 and 600 ºC, pure rhombohedral phase and crystalline Eskolaite structures of Cr$_2$O$_3$ (JCPDS card # 38-1479) were obtained [17,24]. The XRD
The XRD patterns show that all the diffraction peaks are high and broad due to the pure, small size and well-crystallized Cr$_2$O$_3$ 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:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

where $\lambda$ is the X-ray wavelength, $\beta$ is full width at half maximum (FWHM) in radiation and $\theta$ is the diffraction angle of the sharp peak.

Fig. 5 shows the TEM images of the synthesized Cr$_2$O$_3$ nanoparticles and confirmed the size distribution is not homogeneous; nearly rectangle and is in a range of about 10 – 100 nm. By
increasing the temperature to 600 ºC, the Cr₂O₃ nanoparticles obtained were uniform in size and shape (Fig. 5b). A similar result as reported by Su et al. is obtained for the spherical Cr₂O₃ 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 Cr₂O₃ nanoparticles. The curve for Cr₂O₃ nanoparticles prepared at 500 ºC is nearly linear and does not show any magnetic saturation, indicating the paramagnetic contribution [25]. While the curve is not linear for Cr₂O₃ nanoparticles prepared at 600 ºC, it shows a weak ferromagnetic behavior due to the different sizes and shapes of the nanoparticles [26].

CONCLUSION

The Cr₂O₃ 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 Cr₂O₃ nanoparticles obtained at 600 ºC show the better distribution in size and shape. The magnetic properties indicated paramagnetic and weak ferromagnetic nature of the Cr₂O₃ products.
prepared at 500 and 600°C, respectively.

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CONFLICT OF INTEREST
The author declared to no conflict of interest.

REFERENCES