

ABSTRACT

Chromia (Cr₂O₃) nanoparticles have been successfully synthesized via the facile solvothermal process, by using CrO₃ in butanol and propanol as solvents. The functional groups of the samples were tested by the Fourier Transform Infrared (FTIR) spectroscopy. The as-synthesized nanoparticle sizes are calculated and confirmed to be 34 and 40 nm, by using X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). The morphology of the samples was observed by the Scanning Electron Microscopy (SEM). The measured band gap energies ($E_g = 4.04$ and 3.66 eV) higher than that of bulk Cr₂O₃ and increased with decreasing particles size, which indicated that the particles had been successfully synthesized in the nano region, and measured by Ultra-Violet visible (UV-vis) absorption spectroscopy. The broad visible emission at ~ 397 nm, in the photoluminescence spectroscopy revealed the high purity and perfect crystallinity of the samples.)

KEYWORDS: Nanoparticles; Chromia; Structural properties; Optical properties.

I. INTRODUCTION

Nanostructured materials are promising to play a dominant role in future technology as they possess different, and often unique, properties relative to their macroscopic counterparts. Transition metal oxide nanoparticles represent a broad class of materials that have been researched extensively due to their interesting catalytic, optical, electronic and magnetic properties. Metal oxides have attracted much attention recently because of their importance both in science and technology. Among the metal oxide, special attention has been focused on the formation and properties of chromia (Cr₂O₃), which is important in specific applied applications such as in high temperature resistant materials, corrosive resistant materials, liquid crystal displays, green pigment, catalysts [1-5] and so on. It is well known that intrinsic properties of inorganic materials are mainly determined by their composition, structure, crystallinity, size and morphology; great efforts have been devoted to the investigation of different chromia materials synthesis [6-8].

In the synthesis of nanoparticles, among the other methods, the solvothermal process can be used to control the grain size, crystalline phase, particles morphology and surface chemistry, by regulating the sol composition, reaction temperature, pressure, solvent nature, additives and aging time. Nanosized particles prepared using the solvothermal method, are expected to have a larger surface area, smaller particle size, and greater stability than those obtained by other methods. In the present work, we report on chromia (Cr₂O₃) nanoparticles synthesized by the solvothermal process, by using two different solvents. The effects of the solvents on the size and structural, morphological and optical properties of the synthesized nanoparticles have been studied.

II. EXPERIMENTAL PROCEDURE**Synthesis of chromia (Cr₂O₃) nanoparticles**

The synthesis was achieved by means of reagents, all of which were commercially available, analytically pure, and used without further purification.

In the typical procedure, 5 g of CrO₃ (99% purity, Merck) was dissolved in 5 ml of distilled water, which was taken in a 100 ml capacity of Teflon-lined autoclave, then filled with 80 ml of butanol. To obtain the dissolved solution, the autoclave was magnetically stirred for 5 min, and then maintained in a muffle furnace at 150°C for 1h. After it was cooled to ambient temperature, a brownish gel was obtained, which was filtered and washed

with distilled water several times, to remove the soluble impurities. The filtered sample is precursor material, which was dried at 120°C for 5h, then calcined at 500°C for 1h; at the end of the process, the color of the sample was changed from brown to green, and it is named as sample 'a'; the same procedure was followed for the preparation of the propanol mediated sample 'b'.

Characterization of the samples by different techniques

The functional groups of the samples were recorded by Fourier transform infrared spectroscopy on the Nicolet 205 spectrometer in the range of 4000 – 400 cm^{-1} . The crystalline size and structures of the samples were characterized by X-ray diffraction on a rotating-target X-ray diffractometer (SODEBYFLEX 2002). The surface morphologies of the samples were observed by using the Hitachi S-4500 scanning electron microscopy. The particle size and morphology of the samples were further confirmed was examined by JEOL-3010 transmission electron microscopy with an accelerating voltage of 120 kV. The optical absorption spectra of the samples were obtained from a Varian Cary 5E spectrophotometer in the range of 200–800 nm. The photoluminescence emission spectra were carried out on a Fluoromax-4 spectrofluorometer with a Xe lamp as the excitation light source.

III. RESULTS AND DISCUSSION

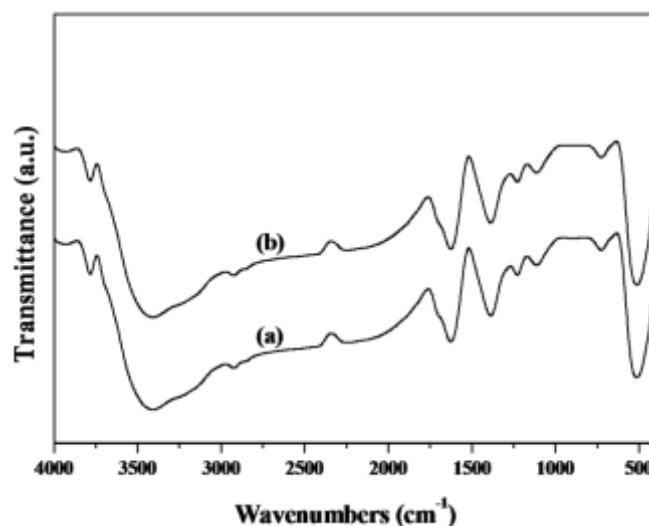


Fig. 1 FTIR spectra of the (a) butanol and (b) propanol mediated chromia samples dried at 120 °C.

FTIR spectroscopy is a useful tool to understand the functional group of the as-synthesized samples. Fig. 1 (a–b) shows the FTIR spectra of samples a and b dried at 120°C. The figure shows that the characteristic bands are 3428, 1628, 1389, 1230, 1114, 728, 520 cm^{-1} , respectively. Among them, 3428 cm^{-1} is due to the OH stretching of non-dissociated water molecules and surface hydroxyls of dissociative chemisorption [9]. 1628 cm^{-1} is due to the bending modes of non-dissociated water molecules, whereas, the absorption bands appearing at 1339, 1230 and 1114 cm^{-1} could be attributed to the hydroxyl groups associated with the Cr^{3+} ions [10]. In the spectra, the bands that appeared at ~728 and 520 cm^{-1} are attributed to the rhombohedral Cr_2O_3 structure [11].

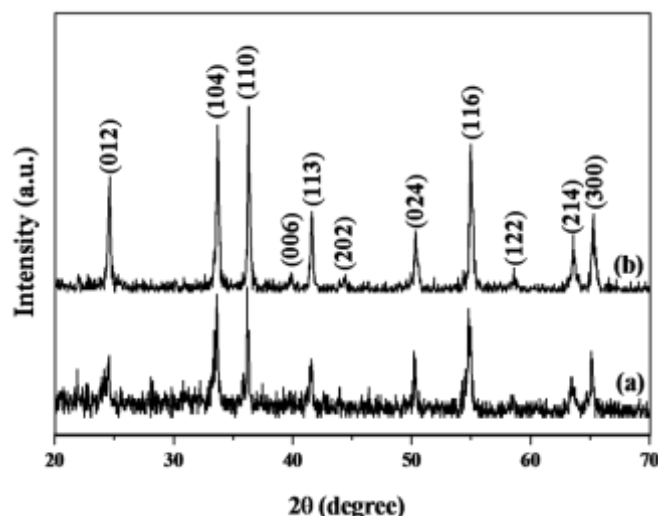


Fig. 2 XRD patterns of the prepared (a) butanol and (b) propanol mediated chromia nanoparticles calcined at 500 °C.

Fig. 2 shows the XRD spectra of the samples. The samples were identified as pure, with well crystallized chromia (Cr_2O_3) nanoparticles, and no extra peak due to impurities was detected. The diffraction peaks were indexed in the rhombohedral structure with an R-3c space group, as described in the JCPDS card (70-3766) [12]. By using the Debye-Scherrer's formula, the average crystallite sizes of the butanol and propanol mediated Cr_2O_3 were found to be 34.54 and 40.22 nm, respectively.

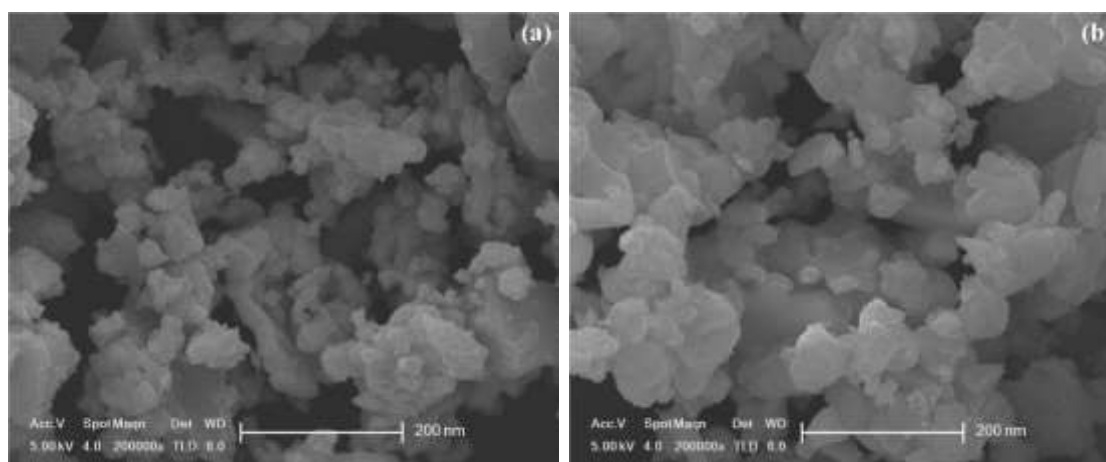


Fig. 3 SEM images of the chromia nanoparticles: (a) butanol and (b) propanol mediated samples calcined at 500 °C.

The influence of the solvents on the morphology of the nanostructures was investigated by the SEM analysis. Fig.3 (a-b) represents the morphologies of the as-synthesized samples a and b, respectively. The SEM images clearly show that the irregular nanostructures were observed for the Cr_2O_3 nanoparticles. However, the butanol mediated sample shows smaller sized nanoparticles, which is probably due to the dispersing ability of the solvent. The TEM analysis was carried out to further confirm the actual size and morphology of the samples. This technology is more direct and less likely to be affected by experimental errors and/or other properties of the particles, such as strain or distribution in the size of the lattice parameter. Fig.4 (a-b) shows the TEM images of samples a and b calcined at 500°C, respectively. It can be seen that, a number of well-dispersed nanoparticles can be clearly seen in the TEM image with an almost even sized distribution, and an external irregular shape for the samples. The particle sizes can be measured directly from the TEM images, which are, to a large extent, well-separated from one another throughout the field of the images, and the particle sizes of samples a and b are irregular, however more number of particles are in nearly uniform and the diameters are 34 and 40 nm, respectively. The results obtained are in good agreement with the particle sizes estimated by XRD analysis using Debye-Scherrer formula.

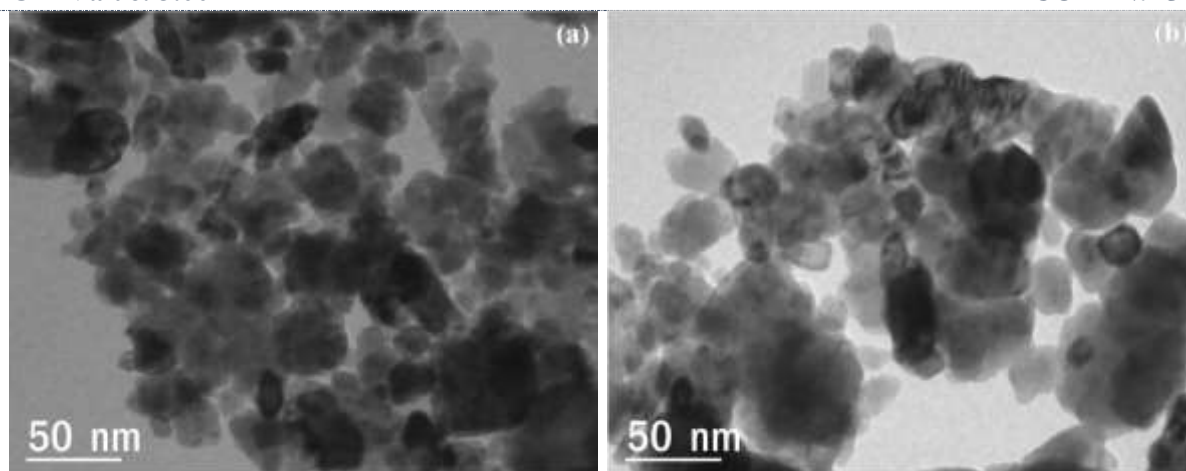


Fig. 4 TEM images of the chromia nanoparticles: (a) butanol and (b) propanol mediated samples calcined at 500 °C.

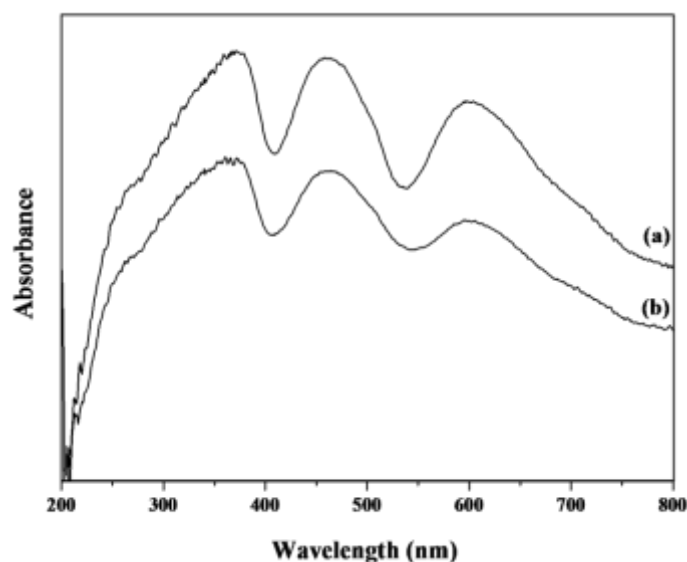


Fig. 5 UV-vis absorption spectra of (a) butanol and (b) propanol mediated chromia nanoparticles calcined at 500 °C.

The optical properties of the products were studied by UV-vis and PL spectra to further assess their quality. With a reduction in the particle size, the band gap of the semiconductor becomes larger, and there is a concomitant blue shift in the absorption spectrum. Fig. 5 (a–b) shows the UV–vis absorption spectra of the Cr_2O_3 nanoparticles calcined at 500°C for the samples a and b, respectively. The absorption spectra showed three broad peaks located at ~360, 450 and 600 nm; among these, the peak at ~360 nm can be assigned to the band gap transition of the Cr^{4+} ions. The other two peaks centered at ~ 450 and 600 nm correspond to the intrinsic ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ d^3 electronic transitions of the Cr^{3+} ions, situated in the six coordinate geometry and octahedral symmetry, respectively [13]. From the absorption data, the optical band gaps (E_g) of the Cr_2O_3 nanoparticles can be estimated by plots of $(\alpha h\nu)^2$ versus photon energy of the Cr_2O_3 nanoparticles, as shown in the Fig. 6. The measured band gap values of the butanol and propanol mediated samples are 4.04 and 3.66 eV, respectively, which are higher than that of the bulk Cr_2O_3 , i.e. 3.4 eV [14].

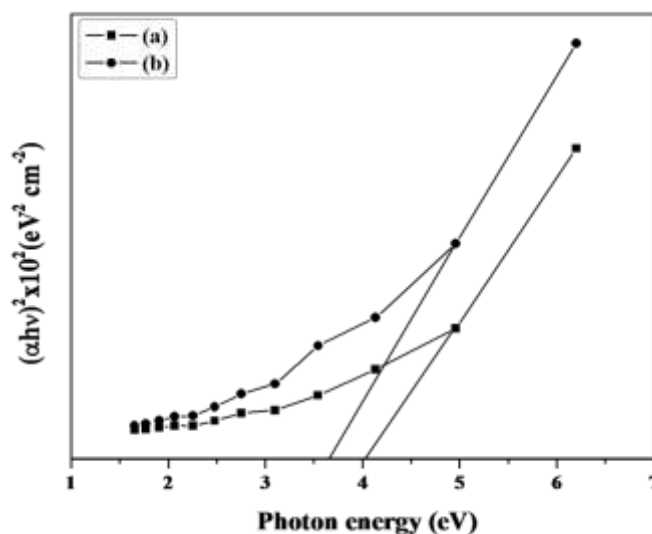


Fig.6 Plots of $(\alpha h\nu)^2$ vs. photon energy of (a) butanol and (b) propanol mediated chromia nanoparticles calcined at 500 °C.

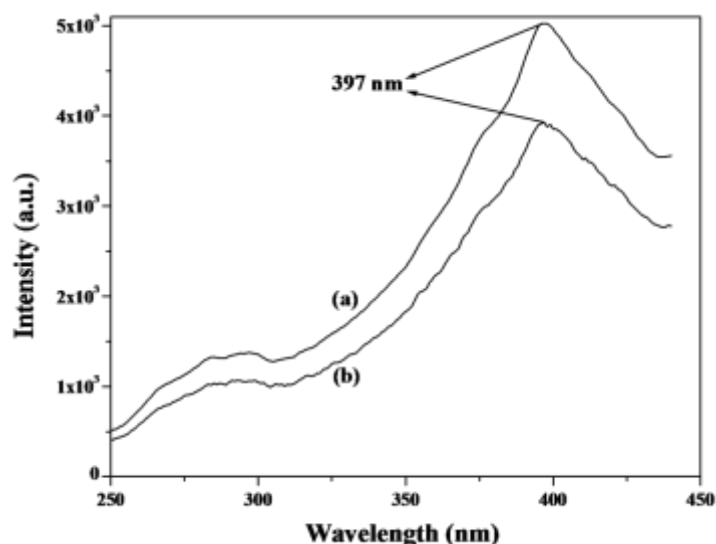


Fig. 7 Photoluminescence emission spectra of (a) butanol and (b) propanol mediated chromia nanoparticles calcined at 500 °C.

Nanostructured materials have a higher density of crystalline defects, such as stacking faults, oxygen defects etc., than their bulk counterparts. In this case, the photoluminescence emission peak can be attributed to such crystal defects within the Cr_2O_3 matrix. The photoluminescence emission spectra of the samples calcined at 500°C were measured at room temperature, as shown in Fig.7 (a–b), for samples a and b, respectively. A broad UV emission peak at ~397 nm dominates in the spectra; it is attributed to the transition involving the $3d^3$ electrons of the Cr^{3+} ions and is ascribed to the perfect crystallinity of the Cr_2O_3 . Moreover, oxygen vacancies are the most dominant defect centers in the oxide materials, and give rise to photoluminescence emission by recombination with an electron, and the peak appears at a lower energy position (higher wavelength region) which may be attributed to the oxygen vacancies. Moreover, it can be seen that the intensity of the peaks differs with the different solvents mediated Cr_2O_3 nanoparticles; the sample ‘a’ was obtained in high intensity, which may be due to the lower crystalline size and presence of the higher oxygen vacancies [15]. Hence, the property of the strong UV emission peak indicates the high purity and perfect crystallinity of the prepared samples. Hence, they are good candidate materials for UV-light emitter using nanolasers, and in optical storage systems in the future [16].

IV. CONCLUSION

In this study, chromia (Cr₂O₃) nanoparticles have been successfully synthesized via the facile solvothermal process. The average particles size of the synthesized samples was confirmed by using the XRD and TEM analyses, which demonstrated that the butanol medium control the size, better than the propanol medium. The morphology was studied by SEM and TEM analyses, which indicates the irregular shape of Cr₂O₃ nanoparticles observed for both the samples. The band gap values of the synthesized samples were found to be 4.04 and 3.66 eV, which are higher than the bulk material. The photoluminescence emission spectra revealed the high purity and perfect crystallinity of the samples, due to the broad emission. Moreover, the prepared Cr₂O₃ nanoparticles are good candidate material for UV-light emitter using nanolasers and in optical storage systems.

V. REFERENCES

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