Synthesis and characterization of Zinc Doped Chromium oxide Nanoparticles by Microwave Irradiation at different concentrations

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Abstract – In this exposure zinc (Zn) doped chromium (III) oxide (Cr_2O_3) nanoparticles are synthesized by simple solvothermal microwave irradiation (SMI) technique. SMI technique is simple and low cost; it has the future to be produced on a huge scale. The effect of dopant (Zn) concentration on the structural behavior of Cr_2O_3 nanoparticles was examined by X-ray diffraction. The average crystallite size of the synthesized nanoparticles was measured from XRD patterns using Scherrer equation and was from ~14 nm to ~16 nm with the increasing Al concentration in Cr_2O_3 from 0 to 5 % (in steps of 0, 1, 2, 3, 5). Almost uniform and hexagonal like morphologies and compositional elements of the synthesized nanoparticles were observed by the field emission scanning electron microscopy (FESEM). The optical property of the samples was measured by ultraviolet - visible (UV-Vis.) absorption spectroscopy. The observed optical band gap value ranges from 2.15 eV to 1.9 eV was highly blue shifted in comparison with that of the bulk Cr_2O_3 (~3.3 eV). This indicated that the synthesized samples are being attributed to the enhancement of the quantum confinement effect.

Index Terms – Cr_2O_3 nanoparticles, SMI method.

1. INTRODUCTION

Nanotechnology is a branch of science which is meant to understand the fundamental physical and chemical properties and the phenomenon of nanomaterials and nanostructures and because of novel application of nanomaterials[1,2]. Nanoparticles can be noncyrstalline, polycrystalline or single crystalline and can be produced with a variety of methods [3].Synthesis of nanomaterials with desired morphology and composition is the most challenging task in the field of nanotechnology. Mostly metal oxides as nanoparticles can exhibit unique chemical properties due to their limited size and high density of corner or edge surface sites [4]. Chromium (III) oxide (Cr_2O_3) nanoparticles have received special attention than the other metal oxide nanomaterials, because of multiple applications including green pigments [5], heterogeneous catalyst[6-8], coating materials for thermal properties [9, 10], solar energy collector [11] digital recording system [12].Because of the high energy density and high capacity at low discharge rates, chromium oxides have been attracted special attention used as cathode materials [13].Meanwhile, doping with selective elements to metal oxides offers an effective method to enhance and control the electrical and optical properties of metaloxide structures[14]. A number of chemical methods of synthesis have been applied to synthesis Cr_2O_3 powders, for example hydrothermal, thermal decomposition [15].

As per green chemistry principles water as an inexpensive, non-toxic,and abundant material in nature, is a safer and ideal solvent for microwave - activated reactions [16,17].

In our study Zn doped Cr_2O_3 nanoparticles are synthesized under microwave irradiation using triethanolamine as template and water as a green solvent. Aqueous solution of Zinc nitrate is used in different concentration at different temperatures to study the effect of concentration in the synthesis of doped nano particles. Synthesis of Zn doped Cr_2O_3 nanoparticles via the microwave irradiation could be worthwhile investigating.

In this paper, we report synthesis of Zn doped Cr_2O_3 nanoparticles by microwave irradiation and its characterization by means of X-ray diffraction (XRD), scanning electron microscope (SEM), UV-Vis and FTIR spectroscopic methods which will give much valuable information about these materials.

2. MATERIALS AND METHODS

All reagents were purchased from S.D. Fine- Chem., and they were used without further purification. Powder XRD patterns of samples were recorded on XPERT-PRO with CuK_α radiation (λ =1.5406A^o) with a scan step time of 10.16s. The average particle size of nanoparticles was determined by using Scherer equation which is given by D = $\frac{K\lambda}{\beta cos\theta}$ where $K$is shape factor (0.89), is the wavelength of x-rays, β is the peak broadening at half maximum (Full width at half maximum intensity -FWHM) and θ is the Bragg angle, Scanning Electron Microscope (SEM) were taken ON VEGA3 TESCAN. Fourier

transformation infrared spectroscopy (FTIR) was acquired with Bruker, Tensor 27 DTGS spectrometer, using KBr pellets. A UV-Vis spectrophotometer CARY 5000 was employed to measure the optical parameters.

3. SYNTHESIS OF Zn DOPED Cr_2O_3 NANOPARTICLES

Aqueous solution of $Cr(NO_3)_3.H_2O$ (0.2M) was mixed with aqueous solution of zinc nitrate $Zn(NO_3.H_2O)$ and appropriate amount of triethanolamine as template (5 ml). After stirring for 40-50 minutes, the mixture was placed under microwave irradiation for 7 minutes. The green solid product was filtered and dried in air at room temperature. The materials were calcinated in electronic oven at 900ºC, for 1 hour. The obtained powder was in green colour.

99% of aqueous solution of chromium nitrate and 1% of zinc nitrate yielded 1% Zn doped Cr_2O_3 nanoparticles. 98% of aqueous solution of zinc nitrate and 2% of zinc nitrate yielded 2% Zn doped Cr_2O_3 nanoparticles. 97% of aqueous solution of zinc nitrate and 3% zinc nitrate yielded 3% Zn doped Cr_2O_3 nanoparticles. 95% of aqueous solution of chromium nitrate and 5% of zinc nitrate yielded 5% Zn doped Cr_2O_3 nanoparticles.

4. RESULTS & DISCUSSION

X-ray Diffraction Analysis

X-ray diffraction (XRD) patterns were collected with an Goniometer=PW3050/60 3000 powder X-ray diffractometer using Cu Kα radiation source (λ = 1.540598 Å), germanium crystal monochromator, at room temperature 25°C, curved position sensitive detector operating at 30 kV and 30 mA. Powder samples were loaded into an sample holder, and each pattern was collected for up to 2 h to obtain sufficiently high signal-to-noise ratio.

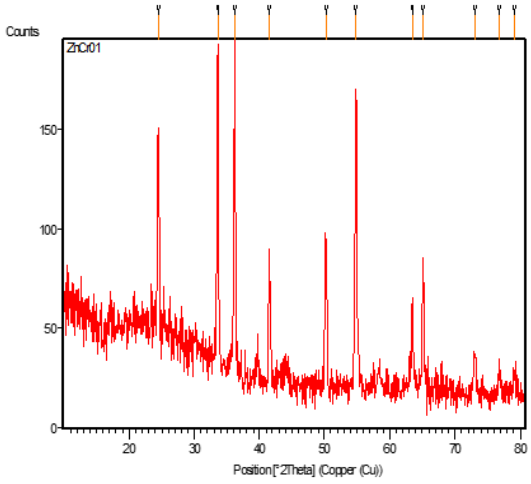

Figure 1: 1% Zn doped Cr_2O_3 nanoparticles

The x-ray diffraction plots of 1% Zn doped Cr_2O_3 nanoparticles, 2% Zn doped Cr_2O_3 nanoparticles, 3% Zn doped Cr_2O_3 nanoparticles and 5% Zn doped Cr_2O_3 nanoparticles are shown in figures 1-4. The average crystallite size of Zn doped Cr_2O_3 nanoparticles are calculated using Scherrer equation.

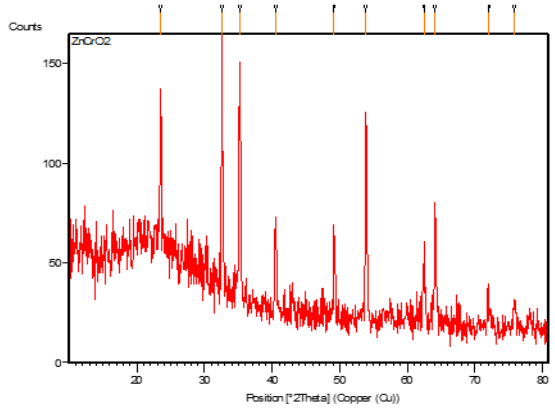

Figure 2: 2% Zn doped Cr_2O_3 nanoparticles

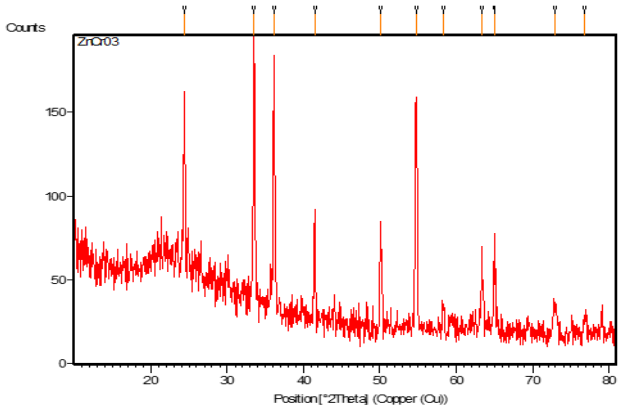

Figure 3: 3% Zn doped Cr_2O_3 nanoparticles

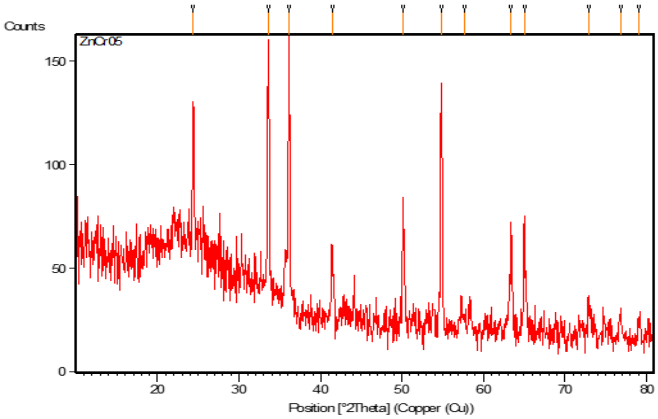

Figure 4: 4% Zn doped Cr_2O_3 nanoparticles

The crystalline size of 1% Zn doped Cr_2O_3 nanoparticles is found to be 14.89 nm. The crystalline size of 2% Zn doped Cr_2O_3 nanoparticles is found to be 15.67 nm. The crystalline size of 3% Zn doped Cr_2O_3 nanoparticles is found to be 16.02 nm. The crystalline size of 5% Zn doped Cr_2O_3 nanoparticles is found to be 16.79 nm.

The average crystallite size increases from 14.89 nm to 16.79 nm for Zn doped Cr_2O_3 nanoparticles as the dopant concentration increases from 1% to 5%. Increase in crystallite size on Zn doping arises due to reduction in the densities of nucleation centres and thus to grow resulting in large crystallites.

SEM studies

Scanning Electron Microscopy and Energy dispersive studies are carried out. Scanning Electron micrographs were obtained using a VEGA3 TESCAN Instrument. The morphological and structural studies are investigated using scanning electron microscopy and displayed in figures 5-8 for 1%, 2% , 3%, 5% Zn doped Cr_2O_3 nanoparticles. These micrographs exhibited the formation of nanoparticles of Zn doped Cr_2O_3 nanoparticles. From the images , it can be considered the particles are bigger in size as the doping concentration of Zn increases which verifies the difference in size from Scherrer formula result.

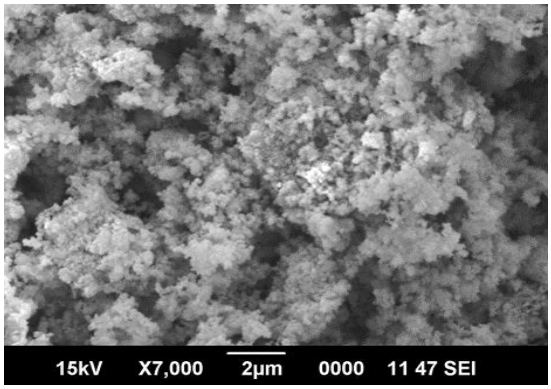

Figure 5 : 1% Zn doped Cr_2O_3 nanopartilces

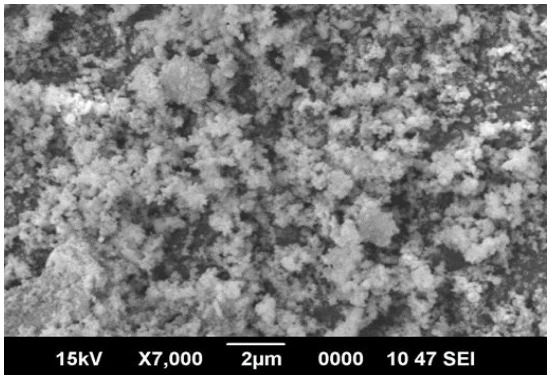

Figure 6: 2% Zn doped Cr_2O_3 nanopartilces

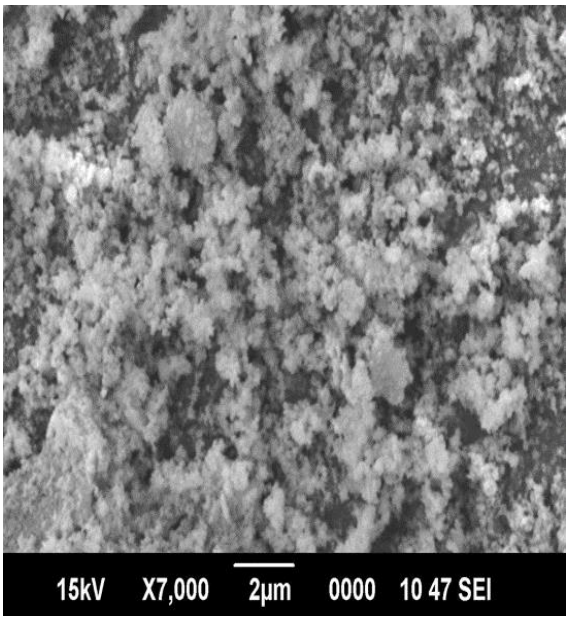

Figure 7 : 3% Zn doped Cr_2O_3 nanopartilces

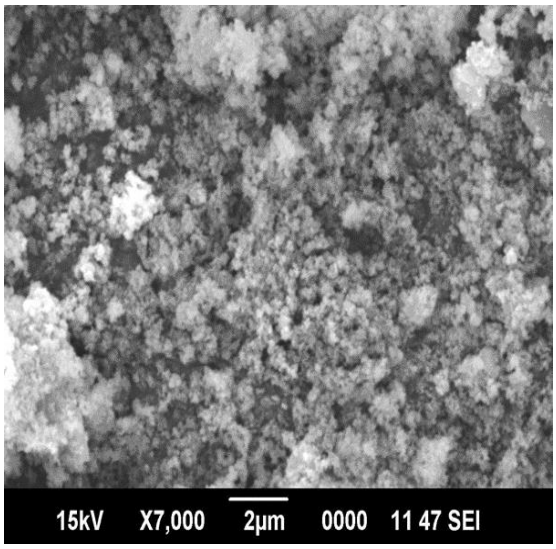

Figure 8 : 5% Zn doped Cr_2O_3 nanopartilces

It was noted that the agglomeration increases with increasing Zn concentration. As the concentration of Zn^{3+} decreases, the size of the particles decreases and at the maximum concentration of Zn^{3+} morphology of the synthesized particles changes drastically into flower like arrangement, this may due to variation in surface atom density of the dopant.

Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectra were recorded in Perkin Elmer 100 spectrophotometer based in Najran University Saudi Arabia. In-order to study the structure and functional group present in the synthesized nanoparticles, FTIR spectroscopy is used.

The FTIR spectra of Zn doped Cr_2O_3 nanoparticles are shown in figures 9-12. The spectrum of 1% Zn doped Cr2O3 nanoparticles shows three sharp peaks at 408.69cm^{-1}, 557.41cm^{-1}, 621.17cm^{-1} due to Cr-O bond and two broad peaks 2923.01 cm^{-1} and 3422.27cm^{-1}. The broad peak at 3422.27cm^{-1} represents stretching of O-H group. In the FTIR spectrum of Zn doped, the Cr-O bands are shifted to lower frequency region because of doping of Zn with Cr_2O_3.

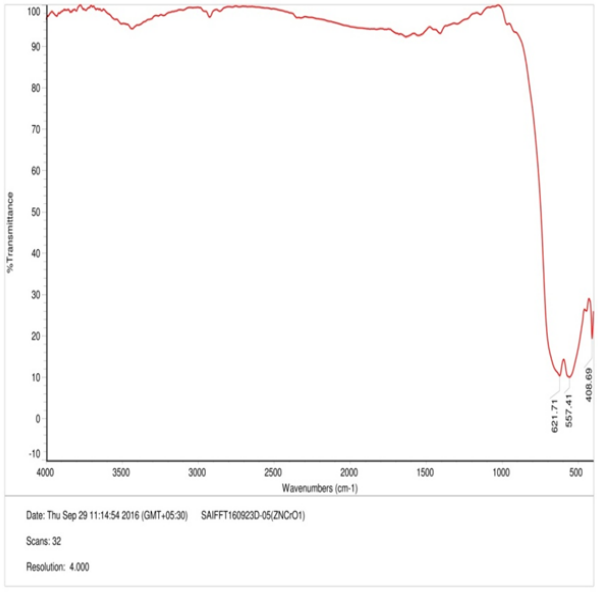

Figure 9: 1% Zn doped Cr_2O_3 nanoparticles

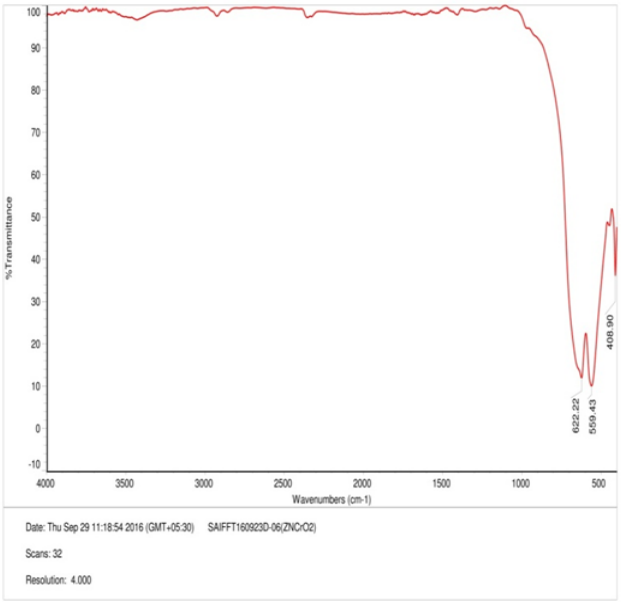

Figure 10: 2% Zn doped Cr_2O_3 nanoparticles

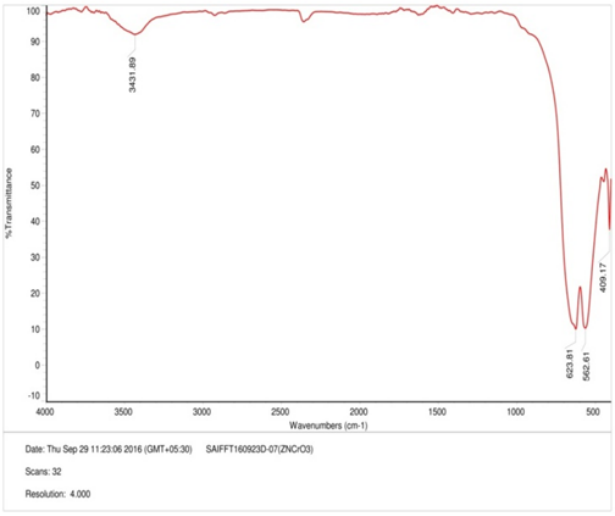

Figure 11: 3% Zn doped Cr_2O_3 nanoparticles

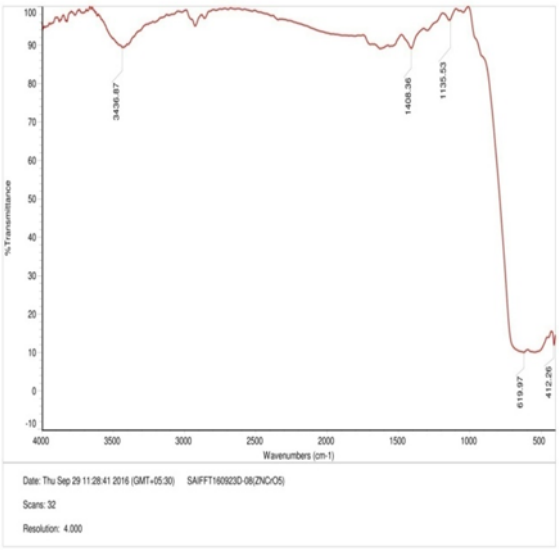

Figure 12: 5% Zn doped Cr_2O_3 nanoparticles

The spectrum of 2% Zn doped Cr_2O_3 nanoparticles shows three sharp peaks at 408.9cm^{-1}, 559.43cm^{-1}, 622.22cm^{-1} due to Cr-O bond and two broad peaks 2920.01 cm^{-1} and 3400.27cm^{-1}. The broad peak at 3400.27cm^{-1} represents stretching of O-H group. In the FTIR spectrum of Zn doped, the Cr-O bands are shifted to lower frequency region because of doping of Zn with Cr_2O_3.

The spectrum of 3% Zn doped Cr_2O_3 nanoparticles shows three sharp peaks at 409.17cm^{-1}, 562.61cm^{-1}, 623.81cm^{-1} due to Cr-O bond and two broad peaks 2918.01 cm^{-1} and 3418.17cm^{-1}. The broad peak at 3418.17cm^{-1} represents stretching of O-H group. In the FTIR spectrum of Zn doped, the Cr-O bands are slightly shifted to lower frequency region because of doping of Zn with Cr_2O_3.

The spectrum of 5% Zn doped Cr_2O_3 nanoparticles shows two sharp peaks at 412.26cm^{-1}, 619.97cm^{-1}, due to Cr-O bond and two additional peaks are appeared at 1135.53cm^{-1} and 1408.36 cm^{-1} and broad peaks 2940.04 cm^{-1} and 3436.87cm^{-1}. The broad peak at 3436.87cm^{-1} represents stretching of O-H group. In this FTIR spectrum of 5% Zn doped, the Cr-O bands are shifted to higher frequency region.

The spectrum of 1% Zn doped nanoparticles, 2% Zn doped nanoparticles, 3% Zn doped nanoparticles, 5% Zn doped nanoparticles are almost same, there is very small change in the frequencies and has little significance during the doping of Zn with nanoparticles.

UV-Visible absorption spectroscopy studies

The spectrum of absorption versus wavelength was recorded in Shimadzu UV Spectrophotometer. Fig.13-16 shows the optical absorption spectra of Zn doped Cr_2O_3 in different concentrations of dopant (Zn) in the wavelength range 0 to 1500 nm. It is observed that the absorbance decreases as wavelength increases.

The UV spectrum of 1% Zn doped Cr_2O_3 nanoparticles shows 5 absorption peaks at 1.367, 1.042, 0.943, 0.610, 0.678 for the wavelength 271 nm, 460 nm, 602nm, 836nm, 1445 nm. The absorption intensity decreases sharply and suddenly for wavelength at 277 nm. This was assigned to increase in the intrinsic band gap of the Zn doped Cr_2O_3 nanoparticles due to high electron transitions from the valence band to the conduction band. Then the absorption intensity decreases slowly as the wavelength increases. Red shift occurs due to increase in the wavelength as compared to UV spectrum of pure Cr_2O_3 nanoparticles.

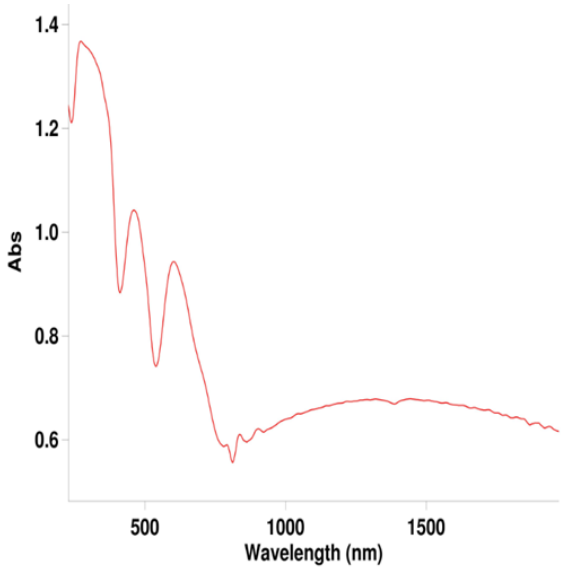

Figure 13: 1% Zn doped Cr_2O_3 nanoparticles

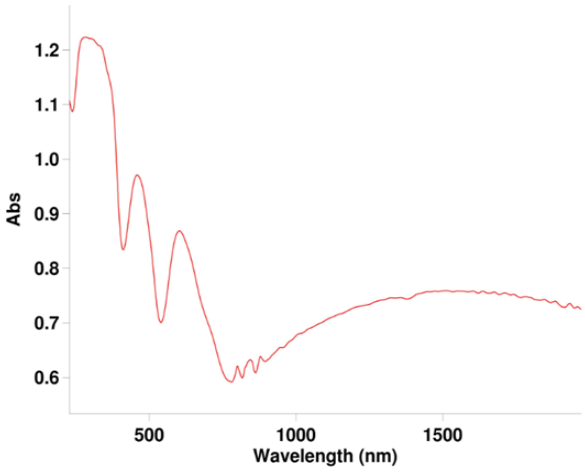

Figure 14:2% Zn doped Cr_2O_3 nanoparticles

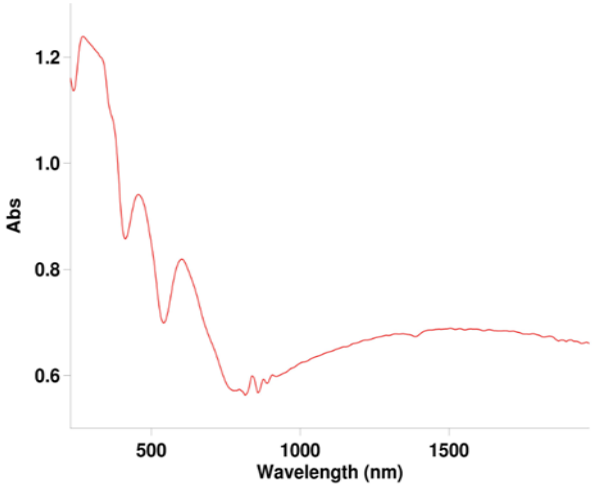

Figure 15:3% Zn doped Cr_2O_3 nanoparticles

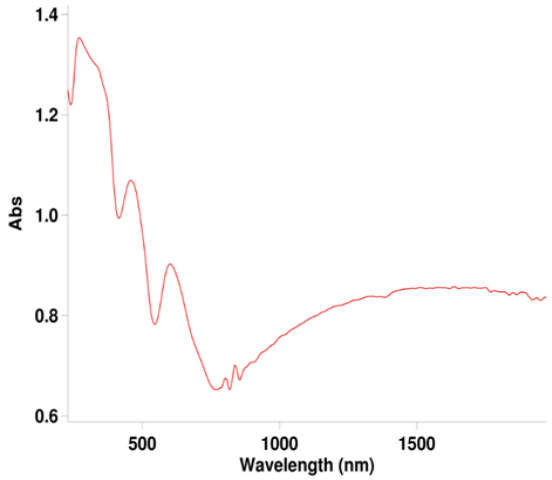

Figure 16 : 5% Zn doped Cr_2O_3 nanoparticles

The UV spectrum of 2% Zn doped Cr_2O_3 nanoparticles shows 6 absorption peaks at 1.224, 0.971, 0.849, 0.621, 0.780, 0.759 for the wavelength 283 nm, 458 nm, 602nm, 800nm, 844nm, 950 nm and 151 nm . The absorption intensity decreases sharply and suddenly for wavelength at 277 nm.

The UV spectrum of 3% Zn doped Cr_2O_3 nanoparticles shows 6 absorption peaks at 1.239, 0.941, 0.819, 0.599, 0.402, 0.689, for the wavelength 270, 456,602, 838, 907, 1506. The absorption intensity decreases sharply and suddenly for wavelength at 270 nm.

The UV spectrum of 5% Zn doped Cr_2O_3 nanoparticles shows 7 absorption peaks at 1.354, 1.069, 0.903, 0.675, 0.702, 0.602, 0.858 for the wavelength 269, 457, 601, 802, 836, 930, 1637. The absorption intensity decreases sharply and suddenly for wavelength at 269 nm.

5. CONCLUSION

In this paper, we have described the synthesis, structural, morphological and optical characterization of a series of Zn doped Cr_2O_3 nanoparticles by simple cost effective solvothermal microwave irradiation technique. Zinc doped Cr_2O_3nano particles were prepared by using chromium nitrate and triethanolamine as template and Zinc nitrate in different concentrations (1%, 2%, 3%, 5%) as the source for Zinc dopant. Regarding the structural properties, a systematic decrease in the unit cell volume, crystallite size, and an increase in the FWHM parameter were observed in concurrence with the presence of Zn dopant in the prepared nanoparticles. The best results were obtained. The structure and phase of the as prepared materials were determined by using the XRD. The average size of the particles was measured by Scherer formula.The morphology and structural analysis was done by the SEM. The particles were found to be porous in morphology. And prepared nano particles were also analysed for FTIR, UV-Visible spectroscopic techniques.

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