Synthesis, FTIR Studies and Optical Properties of Aluminium Doped Chromium Oxide Nanoparticles by Microwave Irradiation at Different Concentrations

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Abstract In this exposure, pure and aluminium (Al) doped chromium (III) oxide (Cr₂O₃) 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 (Al) concentration on the structural behavior of Cr₂O₃ 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 decreased from 14.56 nm to 10.86 nm with the increasing Al concentration in Cr₂O₃ from 0 to 5% (in steps of 0, 1, 2, 3, 5). 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. The optical property of the samples was measured by ultraviolet - visible (UV-Vis.) absorption spectroscopy. The observed optical band gap value ranges from 2.12 eV to 1.90 eV for Al doped nanoparticles and was red shifted in comparison with that of the pure Cr₂O₃ (3.483 eV).

Keywords Cr₂O₃ Nanoparticles, SMI Method, Structural Properties, Optical Properties

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]. The application of nanomaterials utilizes not only chemical composition but also the size, shape and surface dependent properties [3]. Nanoparticles can be noncrystalline, polycrystalline or single crystalline and can be produced with a variety of methods [4]. For the past years, enormous progress in the properties of nanoparticles has been achieved. Nanomaterials, especially transition metal oxides play a specific role in the areas of physics, materials science and chemistry [5]. Synthesis of nanomaterials with desired morphology and composition is the most challenging task in the field of nanotechnology. The synthesis of metal oxides nanostructures have stimulated the great interest because of their novel properties which offers intensive research efforts to fabricate the efficient miniaturized devices for the applications in various nanoelectronics and photononics [6, 7, 8]. Mostly metal oxides as nanoparticles can exhibit unique chemical properties due to their limited size and high density of corner or edge surface sites [9]. Chromium (III) oxide (Cr₂O₃) nanoparticles have received special attention than the other metal oxide nanomaterials, because of multiple applications including green pigments [10], heterogeneous catalyst [11-13], coating materials for thermal properties [14, 15], solar energy collector [16] digital recording system[17]. Because of the high energy density and high capacity at low discharge rates, chromium oxides have been attracted special attention used as cathode materials [18]. A variety of fabrication techniques have been explored in the literature for the synthesis of these metal oxide nanostructures but typically, they can be divided into two categories [19]. Metal oxide nanoparticles are considered to have the potency to generate reactive oxygen species. Band structure is the fundamental material property that controls ROS - producing ability, band turning via introduction of dopants [20]. Meanwhile, doping with selective elements to metal oxides offers an effective method to enhance and control the electrical and optical properties of metal oxide structures [21]. A number of chemical methods of synthesis have been applied to synthesis Cr₂O₃ powders, for example hydrothermal [22], thermal decomposition [23].

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

In our study, pure and Al doped Cr2O3 nanoparticles are synthesized under microwave irradiation using triethanolamine as template and water as a green solvent at different concentrations to study the effect of concentration in the synthesis of doped nano particles. Synthesis of Al doped Cr2O3 nanoparticles via the microwave irradiation could be worthwhile investigating. In this paper, we report synthesis of pure Cr2O3 and Al doped Cr2O3 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: Experimental Procedure

Synthesis of Pure Cr2O3 Nanoparticles

25ml of Cr(NO3)3·H2O (0.2M) aqueous solution was mixed with appropriate amount of triethanolamine as template (5 ml). After stirring for 30-40 minutes, the mixture was placed under microwave irradiation for 4 minutes. The green solid product was filtered and dried in air at room temperature. The materials were calcinated in electronic oven at 200°C, for 1 hour followed by annealation at 500°C, 700°C and 900°C.

Synthesis of Al doped Cr2O3 Nano Particles

Aqueous solution of Cr(NO3)3·H2O (0.2M) was mixed with aqueous solution of aluminium nitrate Al(NO3·H2O) and appropriate amount of triethanolamine as template (5 ml). After stirring for 30-40 minutes, the mixture was placed under microwave irradiation for 4-7 minutes. The green solid product was filtered and dried in air at room temperature. The materials were calcinated in electronic oven at 200°C, for 1 hour followed by annealation. 99% of aqueous solution of chromium nitrate and 1% of aluminium nitrate yielded 1% Al doped Cr2O3 nanoparticles. 98% of aqueous solution of chromium nitrate and 2% of aluminium nitrate yielded 2% Al doped Cr2O3 nanoparticles. 97% of aqueous solution of chromium nitrate and 3% of aluminium nitrate yielded 3% Al doped Cr2O3 nanoparticles. 95% of aqueous solution of chromium nitrate and 5% of aluminium nitrate yielded 5% Al doped Cr2O3 nanoparticles.

3. Results and Discussion

X-ray Diffraction Analysis

X-ray diffraction (XRD) patterns were collected with a Goniometer 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 a sample holder, and each pattern was collected for up to 2 h to obtain sufficiently high signal-to-noise ratio.

Figure 1 shows the XRD pattern of pure Cr2O3 nanoparticles prepared by Cr(NO3)3·9H2O as the chromium source after annealation at 900°C. Based on the XRD pattern, whereas the prepared sample calcined at 200°C proved to be amorphous. The crystallinity of the sample annealed at 900°C was found to be much better than that annealed at 500°C or 700°C. The average crystallite sizes (D) was calculated using well known Scherrer’s equation

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]

where \( \lambda \) is the x-ray wavelength used in xrd (1.54 Å), \( \beta \) and \( \theta \) are the full width at half maxima (FWHM) of the diffraction peak and the Bragg’s diffraction angle respectively. The calculated average crystal size of pure (undoped) Cr2O3 nanoparticles using the above formula based on Table 1 was 14.56 nm and it was compared with previous studies reported as 14.82 nm [26]. The x-ray diffraction plots of 1%, 2%, 3%, 5% Al doped Cr2O3 are shown in figures 2-5. The crystal average size of aluminium doped Cr2O3 nanoparticles were calculated based on the Tables 2-5.

| Pos. [°2Th] | Height [cts] | FWHM Left [°2Th] | d-spacing [Å] | Rel. Int. [%] |
|-------------|--------------|------------------|----------------|--------------|
| 24.51(1)    | 60(8)        | 0.20(4)          | 3.62868        | 55.75        |
| 33.602(7)   | 82(7)        | 0.21(2)          | 2.66494        | 76.23        |
| 36.21(6)    | 95(9)        | 0.19(2)          | 2.47870        | 89.22        |
| 41.49(2)    | 29(6)        | 0.24(5)          | 2.17477        | 27.45        |
| 50.23(1)    | 47(9)        | 0.18(5)          | 1.81479        | 44.10        |
| 54.865(7)   | 107(10)      | 0.20(3)          | 1.67201        | 100.00       |
| 58.41(9)    | 81(10)       | 0.2(2)           | 1.57867        | 7.64         |
| 63.45(3)    | 31(11)       | 0.3(1)           | 1.46488        | 28.71        |
| 65.11(2)    | 40(7)        | 0.22(6)          | 1.43156        | 36.95        |
| 72.97(3)    | 14(2)        | 0.17(5)          | 1.29546        | 13.33        |
| 76.81(3)    | 15(4)        | 0.21(6)          | 1.24001        | 13.95        |
Figure 1. XRD Pattern of Pure Cr$_2$O$_3$

Table 2. Peak list with their relative intensity of XRD of 1% Al doped Cr$_2$O$_3$

| Pos. [°2Th.] | Height [cts] | FWHM Left [°2Th.] | d-spacing [Å] | Rel. Int. [%] |
|-------------|--------------|--------------------|---------------|---------------|
| 23.5116     | 58.06        | 0.1476             | 3.78391       | 99.56         |
| 32.5448     | 58.12        | 0.1476             | 2.75134       | 99.66         |
| 35.1311     | 55.45        | 0.1476             | 2.55449       | 95.08         |
| 40.4649     | 17.73        | 0.2952             | 2.22924       | 30.40         |
| 49.2204     | 21.94        | 0.2952             | 1.85124       | 37.62         |
| 53.8588     | 58.31        | 0.1968             | 1.70225       | 100.00        |
| 62.5259     | 24.08        | 0.2952             | 1.48552       | 41.30         |
| 64.1325     | 28.97        | 0.3936             | 1.45213       | 49.69         |
| 72.0428     | 9.97         | 0.7872             | 1.31092       | 17.10         |

Figure 2. XRD Pattern of 1% Al doped Cr$_2$O$_3$
Synthesis, FTIR Studies and Optical Properties of Aluminium Doped Chromium Oxide Nanoparticles by Microwave Irradiation at Different Concentrations

Table 3. Peak list with their relative intensity of XRD of 2% Al doped Cr₂O₃

| Pos. [°2θ.] | Height [cts] | FWHM Left [°2θ.] | d-spacing [Å] | Rel. Int. [%] |
|-------------|--------------|------------------|---------------|--------------|
| 33.6057     | 35.11        | 0.3291           | 2.66678       | 85.21        |
| 36.1734     | 41.20        | 0.1686           | 2.48324       | 100.00       |
| 54.9401     | 24.43        | 0.3600           | 1.66990       | 59.29        |

Figure 3. XRD Pattern of 2% Al doped Cr₂O₃

Table 4. Peak list with their relative intensity of XRD of 3% Al doped Cr₂O₃

| Pos. [°2θ.] | Height [cts] | FWHM Left [°2θ.] | d-spacing [Å] | Rel. Int. [%] |
|-------------|--------------|------------------|---------------|--------------|
| 23.5072     | 108.23       | 0.1968           | 3.78461       | 75.72        |
| 32.5769     | 137.04       | 0.2460           | 2.74870       | 95.87        |
| 35.2087     | 142.94       | 0.1968           | 2.54904       | 100.00       |
| 40.5507     | 50.78        | 0.1968           | 2.22472       | 35.53        |
| 49.2748     | 65.32        | 0.1476           | 1.84933       | 45.70        |
| 53.8789     | 122.59       | 0.2460           | 1.70167       | 85.77        |
| 62.5157     | 43.75        | 0.1968           | 1.48574       | 30.60        |
| 64.1697     | 67.36        | 0.2952           | 1.45138       | 47.13        |
| 72.1453     | 16.57        | 0.5904           | 1.30931       | 11.59        |
| 75.8994     | 9.25         | 1.1808           | 1.25362       | 6.47         |
| 78.2299     | 9.17         | 0.3936           | 1.22201       | 6.41         |
**Figure 4.** XRD Pattern of 3% Al doped Cr₂O₃

**Table 5.** Peak list with their relative intensity of XRD of 5% Al doped Cr₂O₃

| Pos. [°2Theta] | Height [cts] | FWHM Left [°2Theta] | d-spacing [Å] | Rel. Int. [%] |
|---------------|--------------|---------------------|---------------|---------------|
| 23.4458       | 91.35        | 0.1968              | 3.79438       | 59.27         |
| 32.5640       | 141.82       | 0.1968              | 2.74976       | 92.02         |
| 35.1958       | 154.12       | 0.1968              | 2.54995       | 100.00        |
| 40.4691       | 43.30        | 0.1476              | 2.22902       | 28.09         |
| 49.2920       | 44.28        | 0.2952              | 1.84872       | 28.73         |
| 53.8699       | 115.22       | 0.1968              | 1.70193       | 74.76         |
| 62.5360       | 31.98        | 0.3936              | 1.48531       | 20.75         |
| 64.2682       | 48.67        | 0.3444              | 1.44939       | 31.58         |
| 72.3135       | 7.92         | 1.1808              | 1.30668       | 5.14          |
| 76.1916       | 7.08         | 1.1808              | 1.24954       | 4.60          |
The calculated crystalline average size of Al doped Cr$_2$O$_3$ nanoparticles values are tabulated in Table 6.

| S.No | Concentration of Al | Crystallite average size from Scherrer formula |
|------|---------------------|---------------------------------------------|
| 1    | 0%                  | 14.56                                       |
| 2    | 1%                  | 13.91                                       |
| 3    | 2%                  | 12.86                                       |
| 4    | 3%                  | 12.16                                       |
| 5    | 5%                  | 10.86                                       |

From Table 6, the average size of pure Cr$_2$O$_3$ is observed as 14.56 nm which decreases to 10.86nm as the concentration of Al increases form 1% to 5%. This decrease in average size of nanoparticles with increase of Al concentration due to the increase in the densities of nucleation centers and thus to grow resulting in small crystallites.

**SEM and EDAX Studies**

Scanning Electron Microscopy and Energy dispersive X-ray analysis (EDAX) studies were carried out. Scanning Electron micrographs were obtained using a VEGA3 TESCAN Instrument. Energy dispersive X-ray analysis (EDAX) was used to estimate the composition of the materials using a Bruker CAL 4231 Model attached with Energy Dispersive Spectrometer of EDAX inc. USA.

SEM images of pure Cr$_2$O$_3$ and 1%, 2%, 3%, 5% Al doped Cr$_2$O$_3$ are shown in figures 6-10. These micrographs exhibited the formation of nanoparticles of Cr$_2$O$_3$ and Al doped Cr$_2$O$_3$. From the images it can be considered the particles of Al doped are smaller in size as compared to pure Cr$_2$O$_3$ and the images are well distinguishable also verifies the difference in from Scherrer formula’s result in Table 6. To check the chemical composition of the material, an energy dispersive X-ray (EDS) spectroscopy analysis was performed. Figure 11 shows the EDS spectra of 2% Al doped Cr$_2$O$_3$ nanoparticles which confirm the synthesis of Al doped Cr$_2$O$_3$ nanoparticles. The surface of the Cr$_2$O$_3$ and Al doped nanoparticles also exhibited elements of O, Cr and Al. Here the aluminium is present in elemental form. These results are consistent with the XRD data.
Figure 6. SEM image of Pure Cr$_2$O$_3$

Figure 7. SEM image of 1% Al doped Cr$_2$O$_3$

Figure 8. SEM image of 2% Al doped Cr$_2$O$_3$
Fourier Transform Infrared Spectroscopy Analysis

The FTIR spectra were recorded in Perkin Elmer 100 spectrophotometer based in Najran University Saudi Arabia. The composition and quality of the material was investigated by the FTIR spectroscopy. The FTIR spectra of pure Cr₂O₃ nanoparticles are shown in Figure 12. The spectra shows the Cr-O bond appear at around 450–490 cm⁻¹. The band at around 490 cm⁻¹ may be related with oxygen vacancy or oxygen deficiency in Cr₂O₃. This oxygen deficiency should translate into an enhanced green emission in UV absorption spectra.
The peaks at 1350 cm⁻¹ correspond to the C-O absorption of Cr₂O₃ surface. The weak absorption band at 2367 cm⁻¹ stands for carbonate that probably comes from the atmospheric carbon dioxide during synthesis. The broad peaks around 3429 cm⁻¹ is assigned to the O-H stretching mode of hydroxyl group and 1634 cm⁻¹ (bending) are due to asymmetrical stretching of the chromium carboxylate. The FTIR spectra of 1% Al, 2%, 3%, 5% aluminium doped Cr₂O₃ nanoparticles in different concentration of Al are shown in Figures 13-16. In FTIR studies it is found that there are no significant changes as the concentration of Al increases.

UV-Visible Absorption Spectroscopy Studies

The spectrum of absorption versus wavelength was recorded in Shimadzu UV Spectrophotometer. The optical absorption spectra of pure Cr₂O₃ and 1%, 2%, 3% and 5% Al doped Cr₂O₃ as the function of wavelength ranging from 0 to 1500 nm are shown in figures 17-21.
For pure Cr₂O₃ nano particles, the absorption intensity decreases sharply and suddenly for wavelength at 248nm. This was assigned to the intrinsic band gap of the Cr₂O₃ due to electron transitions from the valence band to the conduction band. Then the absorption intensity decreases slowly as the wavelength increases. After being doped with Al, the absorption peaks shifted towards longer wavelength at 277 nm i.e. red shifted. With doping of aluminium, the absorption spectra shows broadness after the UV peak which might be caused by the surface related defects in the nano particles. The UV emission band is probably due to the radiative recombination of excitons in the surfaces of Cr₂O₃ particles and the visible emission band results from the transition associated with the deep levels due to the oxygen vacancy.

![Figure 18. UV-Vis Spectrum of 1% Al doped Cr₂O₃ nanoparticles](image1.png)

![Figure 19. UV-Vis Spectrum of 2% Al doped Cr₂O₃ nanoparticles](image2.png)

![Figure 20. UV-Vis Spectrum of 3% Al doped Cr₂O₃ nanoparticles](image3.png)

![Figure 21. UV-Vis Spectrum of 5% Al doped Cr₂O₃ nanoparticles](image4.png)

**Band Gap Determination**

The optical band gap of the nanopowders was determined by applying the Tauc relation as given below $\alpha h\nu = B(h\nu - E_g)^n$, where $\alpha$ is the absorption coefficient [$\text{cm}^{-1}$] ($\alpha = 2.303A/t$, here $A$ is the absorbance and $t$ is the thickness of the cuvett), $B$ is a constant, $h$ is Planck’s constant, $\nu$ is the photon frequency, and $E_g$ is the optical band gap. The value of $n = 1/2, 3/2, 2$ or 3 depending on the nature of the electronic transition responsible for absorption and $n=1/2$ for direct band gap semiconductor. An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ on the Y-axis and photon energy $(h\nu)$ on the X-axis (Tauc Plot) gives the value of the optical band gap ($E_g$) as shown in Figures 22-26. The band gap values found from the Tauc plots are shown in table 7 for all samples.
Table 7. Variation in optical band gap with Al concentration

| S.No | Al Concentration | Optical band gap (eV) |
|------|------------------|-----------------------|
| 1    | 0%               | 3.48                  |
| 2    | 1%               | 2.12                  |
| 3    | 2%               | 2.10                  |
| 4    | 3%               | 1.95                  |
| 5    | 5%               | 1.90                  |

From the table 7, the optical band gap for the undoped Cr$_2$O$_3$ is observed as 3.48 eV. On doping with different concentrations from 1% to 5% of Al, Eg value decreases from 3.48eV to 2.12eV.
4. Conclusions

In this paper, we have described the synthesis, structural, morphological and optical characterization of a series of Al doped Cr$_2$O$_3$ nanoparticles by simple cost effective solvothermal microwave irradiation technique. Aluminium doped Cr$_2$O$_3$ nano particles were prepared by using chromium nitrate and triethanolamine as template and aluminium nitrate in different concentrations (1%, 2%, 3%, 5%) as the source for aluminium dopant. Regarding the structural properties, a systematic decrease in the unit cell volume, crystallite size, and changes in the FWHM as the source for aluminium dopant. The morphology and structural size of the particles was measured by Scherer formula for materials were determined by using the XRD. The average volume, crystallite size, and changes in the FWHM structural properties, a systematic decrease in the unit cell 5%) as the source for aluminium dopant. Regarding the aluminium nitrate in different concentrations (1%, 2%, 3%, 5%) as the source for aluminium dopant. The morphology and structural size of the particles was measured by Scherer formula for both doped and pure Cr$_2$O$_3$. The morphology and structural analysis was done by the SEM. Further the presence of aluminium dopants was confirmed EDAX. And prepared nano particles were also analyzed for FTIR, UV-Visible spectroscopic techniques. The optical band values (Eg) values were further obtained from Tauc plots.

REFERENCES

[1] C.N.R. Rao, A. Muller, A.K. Cheetham, “The Chemistry of Nanomaterials: Synthesis, Properties and Applications”. Wilky, Weinheim2004.

[2] A.K. Bandyopadhyay, “Nano Materials: In Architecture, Interior Architecture and Design New Age International”, New Delhi 2008.

[3] T. Pradeep, “Nano: The Essentials, understanding Nanoscience and nanotechnology”, Tata Mc-Graw-Hill Publishing company Limited, New Delhi 2007.

[4] Bihari B., Eilers, H., Tissue, B. M. “Spectra and dynamics of monoclinic Eu$_2$O$_3$ and Eu$_3$+Y$_2$O$_3$ nanocrystals.” Journal of Luminescence1997, 75, 1-10.

[5] Fernandez - Garcia, M. Martinez - Arias, A. Hanson J.C. and Rodriguez, J.A. “Nanostructured oxides in Chemistry. Characteristic and properties.” Chem. Rev. 2004, 104: 4063 – 4104.

[6] S.Y. Bae, H.W. Seo and J.H Park, “Single-crystalline AlZnO nanowires/nanotubes synthesized at low temperature.” J. Phy. Chem. B. 2004, 108, 5206-5214.

[7] Y.J. Chem, J.B. Li et al., “The effect of vapor concentration on the formation of nanowires” J. Cryst. Growth 2002, 245, 163-174.

[8] J.M. Wu, H.C. Shih, W.T. Wn, Y.K. Tseng and I.C Chen. “The Characteristics of low-temperature-synthesized ZnS and ZnO nanoparticles” J. Cryst. Growth2005, 281, 384-391.

[9] Tsoncheva, T. Roggenbuck, J. Paneva, D. Dimitrov, M. Mitov, I. and Froba M. “Nano sized Iron and Chromium oxides supported on mesoporous CeO$_2$ and SBA-15 silica. Physico chemical and catalytic study.” Apply surf. Sci.2010, 257, 523 – 530.

[10] P.M.T. Cavalcante, M. Dondi, G. Guarini, M. Raimondo, G. Baldi, “Colour performance of ceramic nano-pigments.” Dyes pigments, 2009, 80, 226-232.

[11] Rao, T.V.M. Yang, Y. and Sayari A. “Ethane dehydrogenation over pore - expanded mesoporous silica supported chromium oxide. Catalysis preparation and characterization.” J. Mol. Catal. A. Chem., 2009, 301, 152-158.

[12] Rao, T.V.M. Zahidi, E. and sayari. A., “Ethane dehydrogenation over pore-expanded mesoporous silica supported chromium oxide. Catalytic properties and nature of active sites.” J. Mol. Catal. A. Chem.2009, 301, 159-165.

[13] Wang, G. Zhang, L. Deng, J. Hai, H. He, H. and Tong C. “Preparation, Characterization and catalytic activity of Chromia supported on SBA-15 for the oxidative dehydrogenation of iso butane”. Appl. Catal. A. 2009, 355, 192-201.

[14] D. Zhang, B.N. Popov, and R.E. White. “Electrochemical Investigation of CrO$_2$$_5$,doped LiMn$_2$O$_4$ as cathode material for Lithium-ion batteries.” J. Power Sources1998, 76, 81-89.

[15] D. Zhang, P. Arora, B.N. Popov and R.E. White, “Processing, Structure, Property: Performance Investigations of Lithium Manganese-based Oxides for Li Rechargeable Batteries” J. Power sources.1999, 83, 121-132.

[16] Texixeiva, V. Sousa, E. Costa, M.F. Nunes, C. Rosa, L. Carvalho. M.J. Collares - Pereira, M. Roman, E. and Gago J., “Spectrally selective composite coatings of Cr-Cr$_2$O$_3$ and Mo - Al$_2$O for solar energy applications”. Thin solid films 2001,392, 320 - 326.

[17] M.D. Bijker, J.J.J. Bastiaens, E.A. Draaisma L.A.M. Jong, E. Soutry, S.O. Saied, J.L. - Sullivan, “Synthesis and Investigation the Catalytic Behavior of Cr$_2$O$_3$ Nanoparticles”. Nanostructures, 2013, 3, 87-92.

[18] J. Desilverstro, O. Haas, “Solid-state Sodium Batteries Using Polymer Electrolytes and Sodium Intercalation Electrode Materials” J. Electrochem. Soc.1990, 137, 58-65

[19] RaminKarimian, FaridehPiri, “Synthesis and Investigation of the catalytic behavior of Cr$_2$O$_3$ Nanoparticles”. Journal of Nanostructures, 2013, 3, 87-92.

[20] Navid B. Saleh, Delia J. Milliron, NirupamAich, Lynn E. Katz, Howard M. Liliestrand, Mary Jo Kirisits, “Importance of doping, dopant distribution and defects on electronic band structure alteration of metal oxide nano particles. Implications for reactive oxygen species.” Science of the Total Environment, 2016,568, 926-932.

[21] R. Viswananatha, T.G. Venkatesh, C.C. Vidyasagar, Y. ArthobaNayaka, “Preparation and characterization of ZnO and Mg-ZnO nanoparticle”. Archives of Applied Science Research, 2012, 4 (1), 480-486.

[22] J. Zheng, Z.Y. Jiang, Q. Kuang, Z.X. Xie, R.B. Huang, L.S. Zheng, “Shape-controlled fabrication of porous ZnO architectures and their photocatalytic properties”. J. Solid state Chem., 2009, 182, 115-121.

[23] M. Salavati - Niasari, N. Mir. F. Davar“ZnOnanotriangles: Synthesis, characterization and optical properties”. J. Alloys Compd. 2009, 476, 908-912

[24] Dallinger, D. and Kappe, C.O. "Microwave Assisted Synthesis in water as solvent". Chem. Rev. 2007,107, 2563-2591.

[25] Dahd, J.A. Maddx, B.L.S and Hutchison, J.E. “Toward greener nanosynthesis”. Chem. Rev:2007, 107, 2228 – 2269.

[26] F. Farzanesh and M. Najafi, Journal of Sciences, Islamic republic of Iran, 2011, 22(4), 329-333.