

# Optical, Structural, Morphological and Thermal Properties of Mixed $\text{Co}_3\text{O}_4$ - $\text{CuO}$ - $\text{ZrO}_2$ Nanoparticles

<sup>[1]</sup>S. Alwin David, <sup>[2]</sup>C.Vedhi<sup>[1][2]</sup> PG and Research Department of Chemistry, V.O Chidambaram College, Tuticorin, Tamilnadu, India

**Abstract:-** Mixed  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  nanoparticles were synthesized via wet chemical method. Optical, structural, morphological and thermal properties of mixed  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  nanoparticles were studied using UV- DRS, SEM, TEM, TG/DTG and DSC. UV-Vis diffuse reflectance spectrum indicated that the band gap of  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  nanoparticles is about 2.37 - 2.52 eV. The synthesized  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  nanoparticles have irregular morphology with size ranging from 10 - 40nm as evident from SEM and TEM micrographs. TG/DTG and DSC studies revealed good thermal stability of the  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  nanoparticles. From the TG analysis, a total mass loss of only 28.86% was observed in the temperature range from RT to 1200°C.

**Keywords:-**  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$ , Morphology, Band gap, Thermal stability.

## 1. INTRODUCTION

Semiconductor nonmaterial is one of the richest classes of nonmaterial. A semiconductor is a material with electrical conductivity because of electron flow intermediate in extent between that of an insulator and a conductor. Semiconductor has governed a major role in succeeding research in nanoscience and nanotechnology, which consequences in novel classes of semiconductor nanomaterials.

Metal oxide proved to be incredibly promising for a range of handy applications. The good chemical and thermal stability of these inorganic materials facilitate them to be broadly used. Metal oxides take part in a very important role in many areas of physics, chemistry and materials science [1 - 4]. Synthesis of metal oxide nanoparticles is cheaper than the synthesis of metal nanoparticles [5].

Due to the tunable and exceptional characteristics of these metal oxides such as optoelectronic, optical, electrical, magnetic, thermal, mechanical, photochemical, catalytic etc. made themselves admirable candidates for various high level scientific applications. For instance, secondary battery materials, fuel cells, chemical sensors, ceramics, solar cells, gas sensors and biosensor, alkaline and lithium ion batteries, piezoelectric, pyroelectric, ferroelectric, actuator, magnetic, super capacitors, lasers, optical devices, gate dielectric, waveguides, infrared(IR) and solar absorbers, High TC superconductivity, decoupling capacitors dielectrics in dynamics random access memories, magneto- resistance and so on [6 - 10]. Hence metal oxide nanostructure materials have been actively studied in a broader viewpoint by the researchers. Therefore it is necessary to look at its

understanding in immense details interms of their synthesis, properties and applications.

Here in this paper, we will study the synthesis, optical, structural, morphological and thermal properties of mixed  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  nanoparticles.

## 2. EXPERIMENTAL DETAILS

### 2.1. Synthesis of $\text{Co}_3\text{O}_4$ - $\text{CuO}$ - $\text{ZrO}_2$ NPs

About 25mL of 0.1M cobalt(II) chloride was added to the aqueous solution of 75mL of 1.0M sodium hydroxide solution and stirred well. To this mixture 25mL of 0.1M copper sulphate and 25mL of 0.1M zirconium(IV) oxychloride were added. The resulting mixture was stirred well and refluxed at 100 - 110°C for 3 hours. The product was filtered, washed with water and dried. Similar procedure was carried out to synthesize various concentrations of (0.2M - 0.5M)  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs [11].

### 2.2. Characterization

UV-Vis diffuse reflectance spectra were performed with JascoV-600 spectrophotometer. Philips-CM200 Transmission Electron Microscopy (TEM) was utilized to find the shape and particle size of the nanoparticles. The morphology of the nanoparticles was found by JEOL JSM 6390 Scanning Electron Microscopy (SEM). Thermogravimetric (TG), derivative thermogravimetric (DTG) analysis and Differential scanning calorimetry (DSC) were carried out on a NETZSCH STA 449F3 thermal analyzer.

**3. RESULTS AND DISCUSSION**

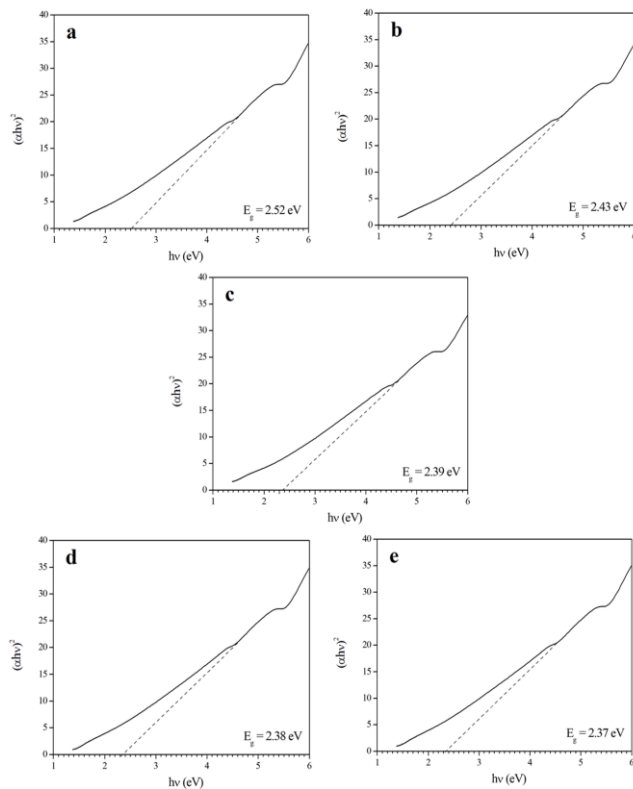
**3.1. Optical properties**

The band gap ( $E_g$ ) of the NPs can be determined using well-known Tauc relation.

$$(\alpha h\nu)^n = A (h\nu - E_g)$$

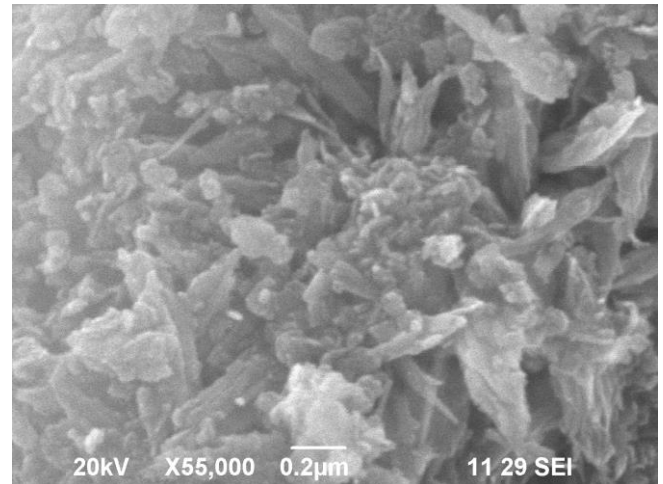
where  $\alpha$ ,  $h$ ,  $\nu$  and  $A$  are the absorption coefficient, Plank constant, light frequency and a constant, respectively. While  $n = 2$  for direct inter band transition. The  $E_g$  value can be estimated by plotting  $(\alpha h\nu)^2$  versus  $h\nu$  and extrapolating the linear part of curve to energy axis at  $\alpha = 0$ .

The band gap energies obtained for the  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs are 2.52eV (0.1M), 2.43eV (0.2M), 2.39eV (0.3M), 2.38eV (0.4M), and 2.37eV (0.5M). This clearly shows that the synthesized  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs has potential as a photocatalyst and excitation of electrons from valence to the conduction band using visible radiation is achievable.



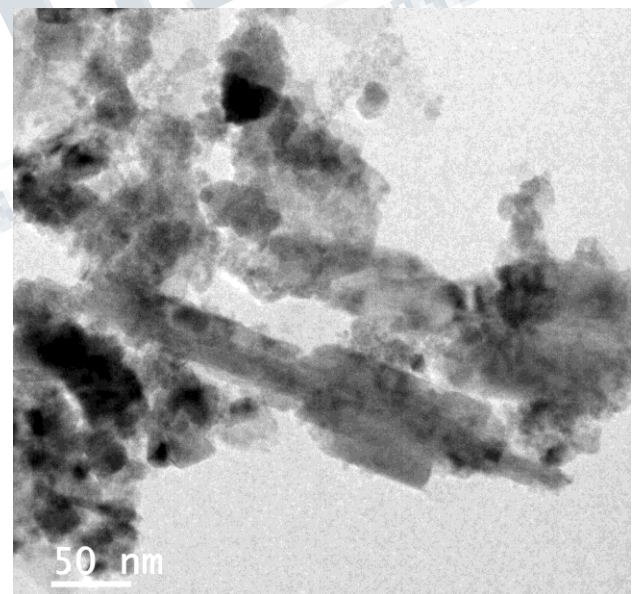
**Figure 1. Plot of  $(\alpha h\nu)^2$  versus  $(h\nu)$  of a) 0.1M  $\text{Co}_3\text{O}_4$ - $\text{CuO}$  -  $\text{ZrO}_2$  NPs b) 0.2M  $\text{Co}_3\text{O}_4$ -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs c) 0.3M  $\text{Co}_3\text{O}_4$ -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs d) 0.4M  $\text{Co}_3\text{O}_4$ -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs e) 0.5M  $\text{Co}_3\text{O}_4$ -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs**

**3.2. Structural and morphological properties**



**Figure 2. SEM image of  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs in 0.2µm scale**

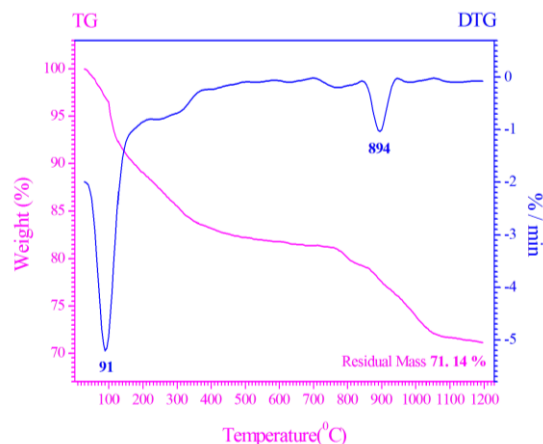
SEM micrographs of  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs is shown in figure 2. The synthesized  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs show granular flakes like morphology.



**Figure 3. TEM image of  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs in 50 nm scale**

TEM images of  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs are shown in figure 3. The  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs show irregular shaped with some rod shaped morphology with 10 – 40nm size.

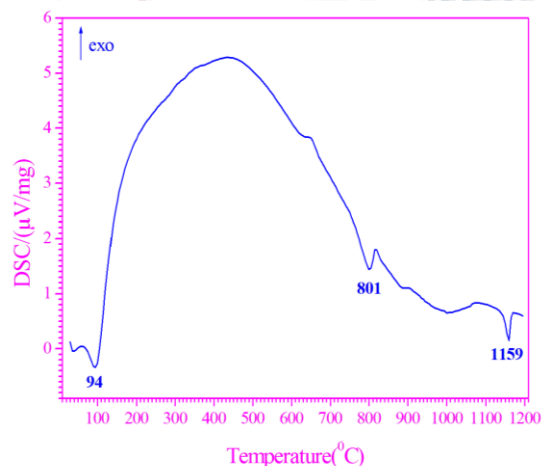
### 3.3. Thermal properties



**Figure 4. TG/DTG Curves of  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs**

The TG/ DTG analysis curve of the as- synthesized  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs is shown in figure (4). Two apparent weight loss steps are observed in the TG curve, accompanied with two peaks at 91°C and 894°C on the DTG curve. This can be ascribed to the removal of water molecules and the degradation of mixed metal oxides, respectively. From the TG analysis, a total mass loss of 28.86% can be observed in the temperature range from room temperature up to 1200°C.

In the case of DSC curve (figure 5), the endothermic peak at 94°C is attributed to the removal of water molecules. When the heating temperature is raised, there are two more endothermic peaks at 801 and 1159°C, indicating the decomposition of mixed metal oxides [12].



**Figure 5. DSC Curve of  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs**

### 4. CONCLUSIONS

Cobalt(II) chloride, copper sulphate, zirconium(IV) oxychloride and sodium hydroxide were used for the synthesis of mixed  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  nanoparticles. The band gap energy values for the  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs are 2.37 -2.52eV, which was calculated by Tauc relation. This results indicated that the synthesized  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs can be used as a photocatalyst in the presence of visible light irradiation. TG/DTG and DSC studies revealed good thermal stability of the  $\text{Co}_3\text{O}_4$  -  $\text{CuO}$  -  $\text{ZrO}_2$  NPs.

### 5. REFERENCES

- [1] Y. Wang, L. Zhou, X. Duan, H. Sun, E. Tin, W. Jin and S. Wang, "Photochemical degradation of phenol solutions on  $\text{Co}_3\text{O}_4$  nanorods with sulfate radicals," *Cataysis Today*, vol. 258, pp. 576–584. 2015.
- [2] S. A. David, V. Veeraputhiran and C. Vedhi, "Synthesis and characterization of  $\text{Co}_3\text{O}_4$ - $\text{ZnO}$ - $\text{ZrO}_2$  ternary nanoparticles," *Journal of Nanoscience and Technolog*, vol. 3(3), pp. 270–272, 2017.
- [3] S. A. David and A. Mathavan, "Thermal, morphological and impedance behavior of Polydiphenylamine- Vanadium pentoxide nanocomposites," *International Journal of Advance Research in Science and Engineering*, vol. 6(1), pp. 262-274, 2017.
- [4] S. A. David, V. Veeraputhiran and C. Vedhi, "Spectroscopic and Morphological Behavior of  $\text{Co}_3\text{O}_4$ - $\text{MnO}_2$ - $\text{ZrO}_2$  Ternary Nanoparticles," *Journal of Nanoscience and Technolog*, vol. 3(4), pp.296–298, 2017.
- [5] S. A. David, K. M. Ponvel, M. A. Fathima, S. Anita, J. Ashli and A. Athilakshmi, "Biosynthesis of silver nanoparticles by *Momordica charantia* leaf extract: Characterization and their antimicrobial activities," *Journal of Natural Product and Plant Resources*, vol. 4 (6), pp. 1-8, 2014.
- [6] S. A. David and C. Vedhi, "Photocatalytic activity of  $\text{Co}_3\text{O}_4$  -  $\text{ZnO}$  -  $\text{ZrO}_2$  ternary nanoparticles for the degradation of methylene blue dye," *International Journal of Advance Research in Science and Engineering*, vol. 6(11), pp. 1914 – 1923, 2017.
- [7] S. A. David and C. Vedhi, "Synthesis of nano  $\text{Co}_3\text{O}_4$  -  $\text{MnO}_2$  -  $\text{ZrO}_2$  mixed oxides for visible-light photocatalytic

**International Journal of Science, Engineering and Management (IJSEM)**  
**Vol 3, Issue 4, April 2018**

---

activity,” International Journal of Advance Research in Science and Engineering, vol. 6(01), pp. 613-623, 2017.

[8] S. A. David and C. Vedhi, “Photocatalytic Activity of Co<sub>3</sub>O<sub>4</sub> - CuO - ZrO<sub>2</sub> Ternary Nanoparticles,” International Journal of Science, Engineering and Management, vol.2 (12), pp. 105-108, 2017.

[9] S. A. David, S. I. Rajadurai and S. V.Kumar, “Biosynthesis of copper oxide nanoparticles using Momordica charantia leaf extract and their characterization,” International Journal of Advance Research in Science and Engineering, vol. 6(03), pp. 313-320, 2017.

[10] S. A. David and L. U. Revathi, “Green synthesis of Fe<sub>3</sub>O<sub>4</sub> nano particles using Camellia angustifolia leaf extract and their enhanced visible-light photocatalytic activity,” International Journal of Advance Research in Science and Engineering, vol. 7(2), pp. 422-428, 2018.

[11] S. A. David and C. Vedhi, “Synthesis and Characterization of Co<sub>3</sub>O<sub>4</sub> - CuO - ZrO<sub>2</sub> Ternary Nanoparticles”, International Journal of Chem Tech Research, vol.10, pp. 905 – 912. 2017.

[12] M. Huang, Y. Zhang, F. Li, Z. Wang, H. Alamusi, Z. Wen and Q. Liu, Q, “Merging of Kirkendall Growth and Ostwald Ripening: CuO@MnO<sub>2</sub> Core-shell Architectures for Asymmetric Supercapacitors,” Scientific reports, vol. 4, pp. 4518, 2014.