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Solid State Characterization of Cu-Zno Nanocomposite Synthesised Via Micro-Wave Irradiation

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----------ABSTRACT----------
The preparation of Cu-ZnO nanocomposite with average crystallite size less than 70nm was carried out successfully using commercial microwave oven operated at a low temperature and pressure (90^0C and 240W) respectively; zinc acetate dehydrate and copper (II) nitrate were used as precursors and ethylenediamine tetracetic acid as complexing agent. Variations of experimental conditions in the microwave such as total period of exposure and irradiation power were found to affect the nanostructures formation. Energy band gap of Cu-ZnO was estimated using absorption data obtained from UV-Vis spectrophotometer. The prepared Cu-ZnO was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX) analysis. Spectra from XRD of Cu-ZnO nanocomposite revealed a hexagonal zincite phase structure and the average crystallites sizes were found to be within the range of TEM result. The XRF analysis revealed the actual elemental composition in the prepared sample. The microwave oven irradiation technique was found to be an effective synthetic method for the preparation of Cu-ZnO nanocomposites and the Cu metal was found to be suitable for coupling with ZnO semiconductor nanoparticle photocatalysis.

KEYWORDS: *AOPs, Cu-ZnO, Microwave, Nanocomposite, Photocatalysis*

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I. INTRODUCTION

The use of ZnO semiconductor in Advanced Oxidation Processes (AOPs) heterogeneous photo catalysis has extensively gained the attention of researchers all over the world owing to its chemical and physical stability, superior magnetic and optical properties, ease of accessibility and high oxidation ability, non-toxic and thermally stable. The presence of large excitation binding energy ~60 MeV and direct wide band gap (3.3eV) in ZnO offers its significance in providing photonic, optoelectronic and spin-based functionality [1-5]. Thus, making its application possible in the field of photo catalysis, gas sensing, and coating in optical devices, solar cells and ceramics [6-10] However, the rapid recombination of the photo excited electron-hole pairs formed during the process of photo catalysis limits the photo catalytic efficiency of ZnO. Therefore, significant efforts have been made to retard this electron-hole recombination in order to enhance photo catalysis by coupling the nanocomposite with other materials such as metals, semiconductors and carbon nanotubes [10-13]. The Cu nanocomposite on the surface of ZnO can act as a sink for electrons hence improving the electron-hole separation. Since the rate of electron transfer from valence band to conduction band of deposited Cu on ZnO is expected to be faster as compared with electron-hole pair recombination, then, the can effectively separate the excited electron-hole pairs. Several methods have been reported for the synthesis of metal/ZnO nanocomposites such as chemical bath deposition, hydrothermal method, photo reduction method, sol-gel method, non-ionic polymer assisted thermolysis and so on. However, most of these methods are limited to research purposes because of either the use of toxic reagents, high temperature, high pressure, expensive equipment or long reaction period. It is noticeable that a simple and more effective route for the synthesis of Cu-ZnO nanocomposite is still required to meet both economic and industrial needs. The introduction of microwave (MW) irradiation into the synthesis process of Cu coupled ZnO assist in the enhancement of the production of a nanocomposite with small and narrow inorganic particle size distribution and improved photo catalytic efficiency in a short reaction time with high purity [14-16].

In this study, a single-step solution phase assisted microwave technique is reported for the preparation of pure ZnO and Cu-ZnO nanocomposite respectively at very low temperature 90^{o}C and power 240W using EDTA and PVA as co-ordinating and binding agent respectively without any requirement for post annealing treatment or any surfactant. This makes the method suitable for industrial production.

II. MATERIALS AND METHOD

Zinc acetate dihydrate [Zn $(CH_3OO)_2{\cdot}2H_2O$] (>99% Merck), EDTA [C10 (>99% Merck), ethanol C_2H_5OH (> 99% Merck), copper (II) nitrate (> 99% Merck), deionised water. All the chemicals were used in this study as received without further purification and commercial microwave oven was employed as the source of heat.

2.1 Preparation of samples

In a typical preparatory procedure, 11g Zn $(CH_3OO)_2.2H_2O$ and 2.1g $CuNO_3$ were dissolved into 80ml and 20ml deionised water respectively under agitation. Obtained solution were the mixed together in a 250ml conical flask and agitated for 2mins, 0.9g EDTA was dissolved in 20ml deionised water and was added into the mixture of solutions 1 & 2 in drop wise manner under agitation. The mixtures were the transferred into Teflon reaction vessel was irradiated in the microwave oven for 10mins at 90^{0}C and 240W. Samples were then removed from the microwave and allowed to cool down naturally. After which deep blue crystals were formed and was separated by microfiltration, washed several times with ethanol absolute and deionised water. The obtained crystallite sample was dried in the oven for 6hrs at temperature of 60^{0}C.

2.2 Characterization of the Nanocomposite

The crystal phase purity, average crystallite particle size and crystallinity of the prepared Cu-ZnO was analysed using XRD-X`PERT PRO PW3040 diffraction meter, having Cu-Kα radiation (λ=1.54Å) operating at room temperature. Investigation of sample morphology was carried out under the Field Emission Scanning Electron Microscopy (FESEM/EDX-HITACHI H7100); the compositional analysis of the samples was obtained using energy-dispersed EDX. Additionally, the functional groups characterization of the ZnO and Cu-ZnO nanocomposite was analysed using Fourier Transform Spectrophotometer (FT-IR Perkin Elmer 100 series spectrophotometer). Transmission electron microscopy (TEM) was also performed with Hitachi H-7000 operated at 30μA and 100kV. Band gap was evaluated using absorption data from UV-VIS-NIR spectrophotometer (UV-3600 Shimazu).

III. RESULTS AND DISCUSSION

3.1 Structural Analysis

Figure 1**:** Shows the XRD pattern of pure (a) ZnO and (b) Cu-ZnO nanocomposites. From Figure 1a, it indicates that all the observed peaks belongs to ZnO and is in accordance with the International Centre for Diffraction Data hexagonal zincite structure of ZnO (Reference Code; 98-005-2842). The peaks observed shows high purity of the as-prepared ZnO nanocomposite with 99% crystalline phase evaluation with no impurity. An average crystallite size of (D) <70 nm was estimated using Sherrers equation; $D=\frac{k\lambda}{BCos\theta}$ where λ=wavelength $(1.54A^{o})$ K=constant 0.94 & B = FWHM at 2θ.

Figure 1b shows that, the powders obtained from the microwave preparation typically contain 75% hexagonal zincite ZnO (Reference Code: 98-004-0985). It also exhibits a typical pattern of face- centred-Anorthic Cu metal and is consistent with values of (Ref Code: 98-011-5831). There were no peaks of CuO which indicate that the Cu-ZnO nanocomposite can be obtained using the microwave irradiation method and the ZnO nanocrystal lattice parameters change is negligible. While other crystalline phases where mainly due to C & O.

Figure 2: Shows the TEM images of the synthesized (**a)** ZnO and (**b**) Cu-ZnO nanocomposites, with observed rod-like shapes having diameters in nanometre range less than 70nm.

The average crystallite size obtained using the Scherrer equation was <70 nm which is found to be within the range of size obtained from TEM results.

3.2 Elemental and Morphological studies

Samples morphology of pure ZnO and Cu coupled ZnO nanocomposites were characterized by FESEM and EDX as shown in Figure 3a, 3b, and Figure 4 respectively. The FESEM images of pure ZnO and Cu coupled ZnO derived from Zn (CH3OO)2·2H2O where depicted in Figure 3a and from (ii) the particles were found to agglomerate and formed bundles of nanorods with different lengths and diameters indicating wide range of uneven and size distribution. The ends of the rods were found to be hexagonal in shape and bundle formation of smaller and shorter nanorods reveals rapid nucleation with high particle growth inhibition. As observed from the images in Figure 3b (i), there is no actual definite shape and size of the images. While the

high magnified image of the coupled Cu-ZnO morphology can be observed to have almost homogenous nanorod shape diameter distribution. The elemental composition of the prepared samples obtained from the EDX integrated together with the FESEM machine confirms the presence of Zn, O and Cu as well as their composition. The EDX images illustrated that the composition of the selected areas contain only pure elements of the Zn & O as in Figure 4a and Zn, O & Cu in Figure 4b. This confirms the purity of the samples, other minor signals where confirm to be only due to equipment vibration.

3.3 Molecular vibrational Study

The pure ZnO and Cu coupled ZnO (Cu-ZnO) Nanocomposites FT-IR spectra were recorded using the FT-IR spectrometer between the ranges of 280cm-1 to 4000cm-1 as shown in Figure 5. In the Cu-ZnO Nanocomposite spectrum, various functional groups and metal-oxide bonds were observed in the compound. In the spectrum of pure uncoupled ZnO nanocomposite powder, absorption band at around 400cm-1 indicates the presence of Zn-O which was also observed in the coupled Cu-ZnO nanocomposite spectrum. The broad band in the coupled Cu-ZnO at ~690 cm-1 is assigned to the characteristic stretching mode of Cu-O, while other absorption bands found around 1036, 1430, and 1599 cm-1 are mainly due C=C, C-H and C=O stretching. Absorption band observed at ~3371 cm-1 arises due to the O-H group stretching mode indicating the presence of some absorbed water by the nanostructure [17-20].

3.4 Elemental composition

Table1&2 shows the elemental composition of both main and trace elements in the MW synthesized Cu-ZnO and ZnO nanocomposite respectively verified by XRF analysis. Generally, results obtained by XRF depend on combination of errors contributed by the method of sample preparation and measurement of both the background intensities with peak value [17]. From the XRF analysis based on quantitative indication of analyte composition, the nanocomposite was found to contain 72% Zn and 27% Cu.

3.5 Optical Studies: UV-VIS-NIR spectrophotometer was used to measure the absorbance of the synthesized nanocomposites at room temperature in the wavelength range 220-800nm and band gap absorbance edge was found to appear at (384nm) for uncoupled ZnO and (390nm) for Cu-ZnO coupled nanocomposite respectively. They are all within the visible region, the band gap energy which is the photon energy at which transition between absorption and non absorbing behaviour takes place is determined as 3.23eV and 3.18eV for ZnO and Cu-ZnO by linear fitting of the sample absorption spectra edge which the transition region is observed in Figure 6 (a&b).

3.6 Effect of Cu Coupling on ZnO: The coupling effect of Cu on the photo-catalytic activity of ZnO photo-catalyst may be caused from several reasons as previously discussed for Ag doped TiO_2 [18]. The excessive coverage of metals on ZnO may limit the light reaching the surface of ZnO thus, leading to the decrease in the amount of photo-generated electron-hole/pairs, and in turn caused a decrease in photo-catalytic activity of ZnO semiconductor photo catalyst [19]. For the desired photo-catalytic reaction, the metal can occupy the surface active site of ZnO, thus, causing the reduction of photo-catalytic activity of metal coupled ZnO. Therefore, making the probability of the hole captured to be increased by particles of metal loading content which is high, hence the probability of the holes to react with the absorbed specie i.e. H_2O_2 or H2O becomes decreased [20]. The hybrid orbital of oxygen-1s can shift to higher energy level which is higher thus, indicating increase in the content of OH and decrease in the photo-catalytic activity. While surface photo voltage spectroscopy (SPS) decreases which means that photo-induced electrons can easily be removed by adsorbed oxygen through the clusters of the noble metal hence, inhibiting the photo induced electron-hole pair recombination. Semiconductor coupled photo catalysts can provide an efficient and interesting photo-catalytic process by increasing the charge separation and extending the range of photo-excitation for the system.

IV. FIGURES AND TABLES

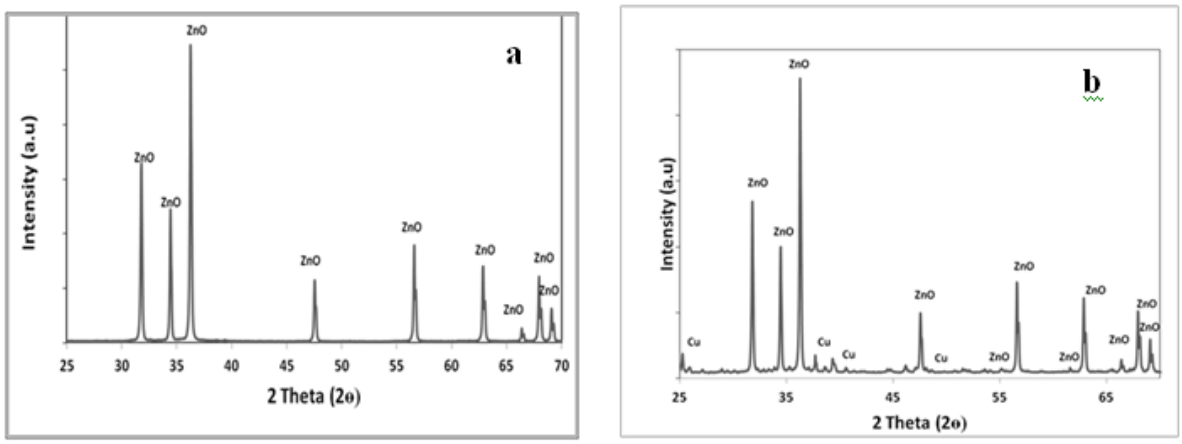

Figure 1: XRD patterns of (a) Pure ZnO Nanocomposite & (b) Cu- ZnO Nanocomposite

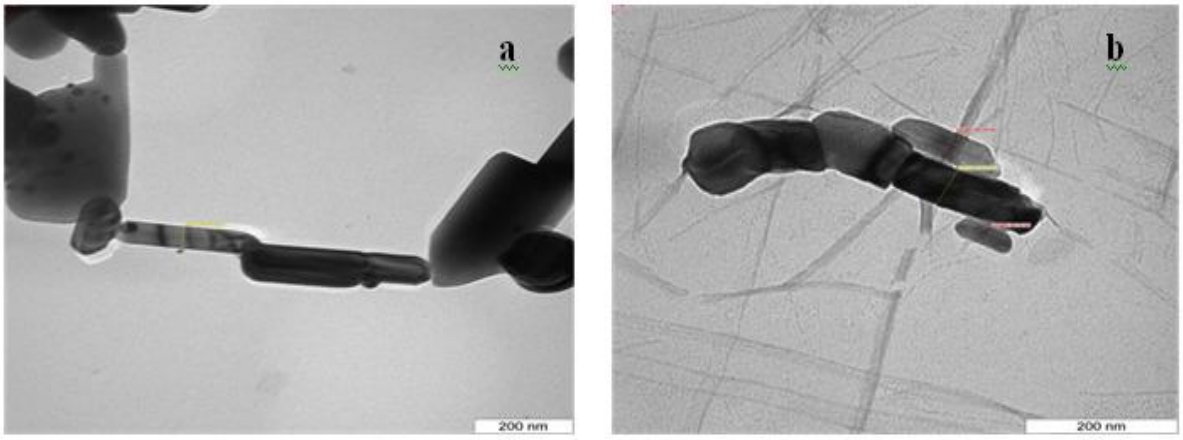

Figure 2: TEM images of MW synthesized (a) ZnO and (b) Cu-ZnO Nanocomposites

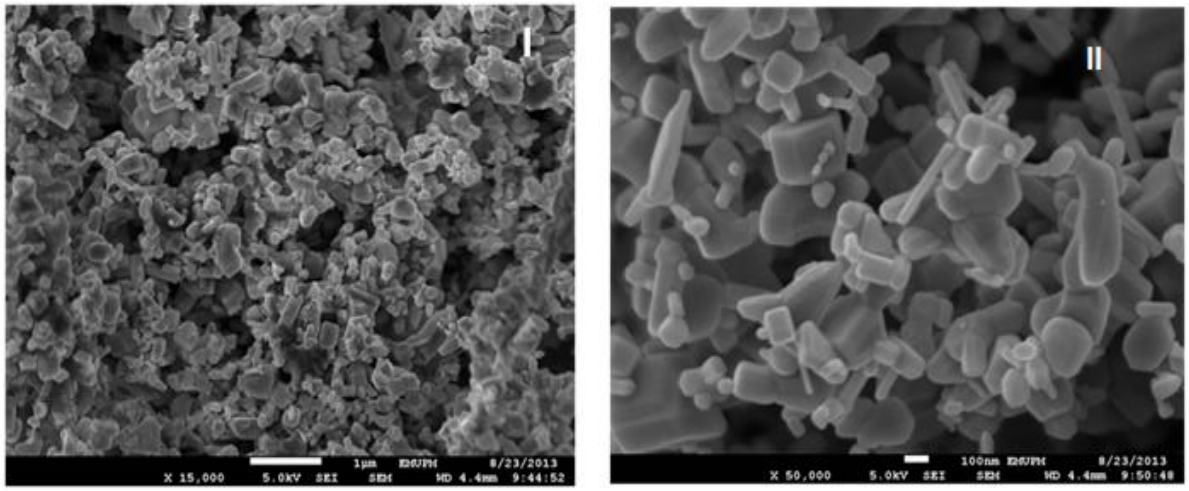

Figure 3a: low (i) and high (ii) magnified FESEM images of select areas of pure MW synthesized ZnO nanocomposite.

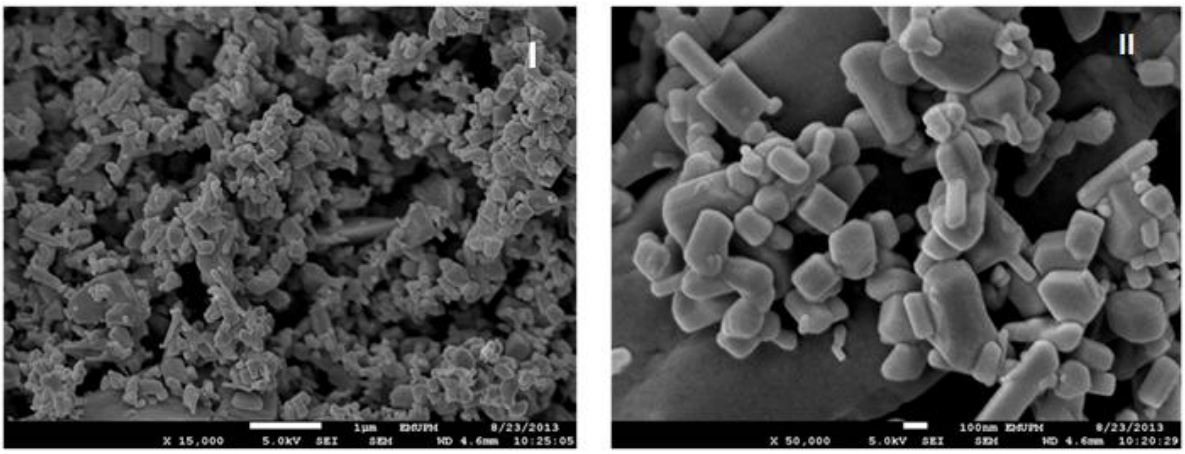

Figure 3b: Low (i) and high (ii) magnified FESEM images of select areas of MW synthesized coupled Cu-ZnO nanocomposite

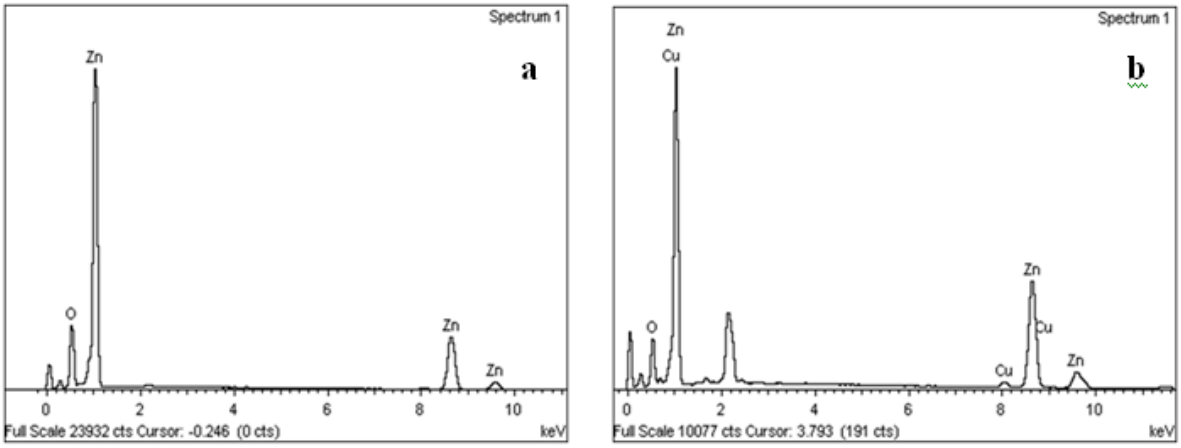

Figure 4: EDX Images of the selected areas of MW synthesized (a) ZnO and (b) Cu-ZnO Nanocomposite

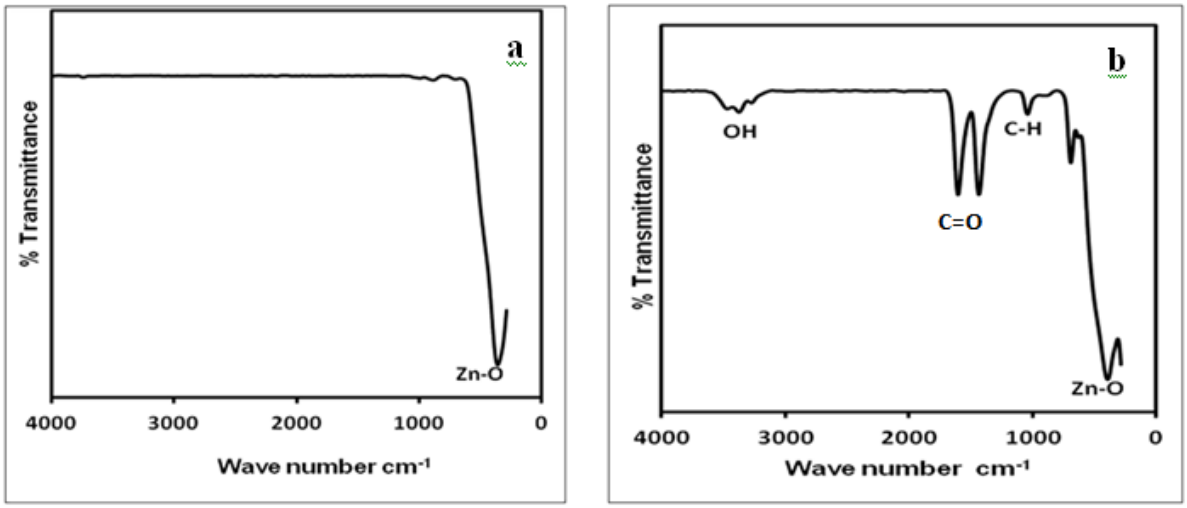

Figure 5: FT-IR spectra of MW synthesized (a) ZnO Nanocomposite and (b) Cu-ZnO Nanocomposite.

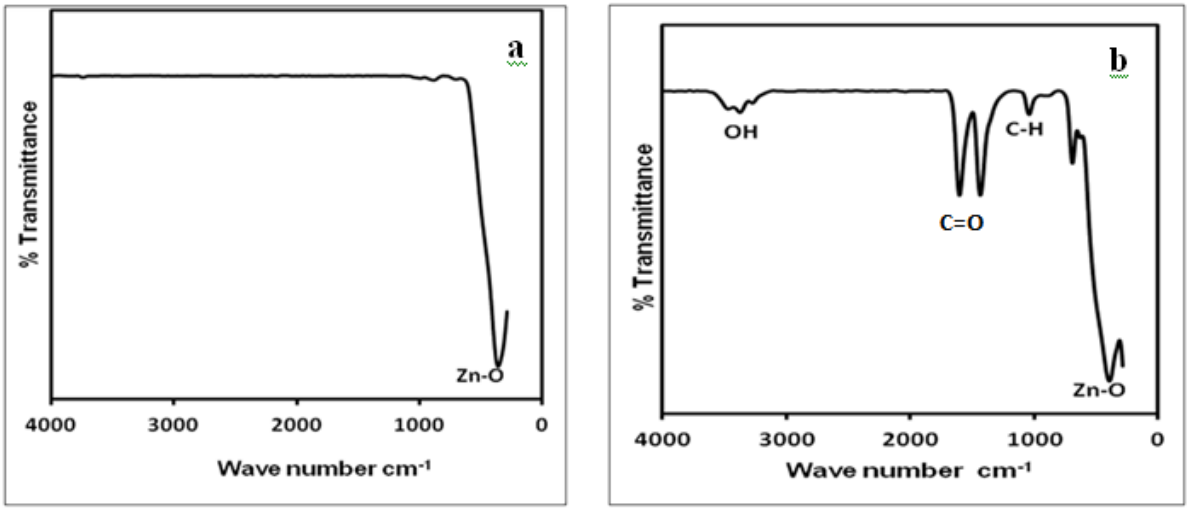

Figure 6: Band gap energy estimation for (a) MW Synthesized ZnO and (b) MW-Synthesized Cu- ZnO Nanocomposites

Table 1: Quantitative Result of XRF Analysis for MW-Synthesized Cu-ZnO Nanocomposite

Analyte	Result (%Mass)	Std.Dev.	Proc.-Calc.	Line	Intensity(cps/uA)
Zn	72.088	0.063	Quan-FP	Zn-Ka	1482.6703
Cu	27.402	0.038	Quan-FP	Cu-Ka	567.8831
Ca	0.418	0.007	Quan-FP	Ca-Ka	0.3195
Ni	0.092	0.003	Quan-FP	Ni-Ka	2.9802

Table 2: Quantitative Result of XRF Analysis for MW-Synthesized ZnO Nanocomposite

Analyte	Result(%Mass)	Std.Dev.	Proc.-Calc.	Line	Intensity(cps/uA)
Zn	99.654	0.072	Quan-FP	Zn-Ka	2051.7066
S	0.171	0.014	Quan-FP	S-Ka	0.0300
Ni	0.110	0.003	Quan-FP	Ni-Ka	4.2757
Ca	0.065	0.003	Quan-FP	Ca-Ka	0.0494

IV. CONCLUSION

The Cu-ZnO nanocomposite was successfully synthesized using microwave irradiation method at low temperature of 90^0C without using any surfactant and no post annealing treatment. The crystallinity of the nanocomposite was controlled by EDTA as complexing agent. Confirmation of sample structural, elemental composition, morphology, optical and molecular vibration properties were investigated using XRD, TEM, XRF, FESEM, EDX, and FT-IR. Microwave oven irradiation technique was found to be an effective synthetic method for the preparation of Cu-ZnO nanocomposites and the Cu metal was suitable match for ZnO semiconductor nanoparticle photo catalysis.

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