

Biosynthesis of MO-MCo₂O₄ [M=Zn and Cu] Composites from peel extract of pomegranate fruits - 'Punica granatum'

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ABSTRACT: The bi-products of general physical and chemical synthesis methods are environmentally hazardous and, above all these processes of synthesis are expensive. On the other side, use of plant extract or fruit extract under biosynthesis methods are chosen at present to prepare nano materials. In the present work, we report the synthesis of two composite ceramics MO-MCo₂O₄ [M=Zn and Cu] under microwave assistance clubbed with biosynthesis. Metallic salts along with the *punica granatum* peel extract as fuel are taken as precursors for microwave irradiation. As prepared products are annealed at 700 °C for 3 h and leads to dark colored MO-MCo₂O₄ [M=Zn and Cu] composite powders. The samples are characterized for their structural properties under powder X-ray diffraction (PXRD), scanning electron microscopy (SEM). The optical properties are characterized under diffuse reflectance spectroscopy (DRS), photoluminescence (PL) spectroscopy and Fourier transform infrared spectroscopy (FTIR). The powder XRD analysis have confirmed their chemical composition. In addition, band gap energy was calculated from Tauc's plot and is observed at 5.6 and 5.5 eV, these values are high compared to the previous literature.

KEYWORDS: MO-MCo₂O₄ [M=Zn and Cu], 'ZnC' (ZnO-ZnCo₂O₄), 'CuC' (CuO-CuCo₂O₄), microwave assisted synthesis, Punica granatum, characterization, photoluminescence.

I. INTRODUCTION

Spinels are the heterometallic oxide compounds with a general formula of MN₂O₄, in which M and N are divalent and trivalent metals respectively. Transition metal spinels are considered to be promising materials for catalytic applications such as catalytic combustion of hydrocarbons, oxidation of CO, selective oxidation or reduction of organic compounds [1]. MO-MCo₂O₄ [M=Zn and Cu], that comes under transition metal spinels family, with a cubic spinel structure. In these spinels Zn and Cu ions are present in the tetrahedral sites and trivalent Co ions occupying the octahedral sites of the cubic spinel structure [2]. The p-type semiconducting behaviour of ZnCo₂O₄ has promoted its use in organic photovoltaic's as a hole transporting layer [3]. In recent years ZnCo₂O₄ nanoparticles are used in the area of gas detectors for the detection of harmful gases such as SO₂, CO, Cl₂, NO₂, CH₃COOH, C₂H₅OH and LPG [4] [5]. Similarly the CuCo₂O₄ nanoparticles are used in catalytic oxidation of CO and CO₂, pollution control in automobile and alcohol synthesis [6, 7]. Investigators also used the CuCo₂O₄ nanostructures as an anodic material in the Li-ion batteries and suggested that they offer high-charge storage capacity through redox reactions [8].

On the other hand, ZnO and CuO are the simple metal oxides, that attracted the interest of the investigators with their wide applications among the fields of pharmaceuticals, agro chemicals, cosmetics, ceramics, and optics [9]. The important properties of ZnO are the piezo and pyroelectric properties, for the same it is used in piezoelectric

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transducers, sensors, and piezo-electronic devices, etc. [10]. In addition both the metal oxides and heterometallic spinels are showing electrical properties and electronic application, hence the combination of both may show better performance. Hence it is considered that the mixed oxide –spinel for example ZnO-ZnCo₂O₄ (ZnC) and CuO-CuCo₂O₄ (CuC) may show the promising possibility as an anode material in the lithium ion batteries (LIB's). Due to the presence of high content of metal, i.e. Zn and Cu in the bi-component ZnC and CuC that can offer higher capacity by alloying/dealloying reactions between metal Zn, Cu with that of Li. Besides, the presence of Co may enhance the higher and stable capacity of LIB's in the form of mutually beneficial matrix ions in the lithiation/delithiation process [11].

To the best of our knowledge the production of bi-component ZnC and CuC with smart architecture is a challenging process, till to the date. Various synthesis techniques are available for the production of ZnCo₂O₄, CuCo₂O₄, ZnO and CuO. Some common methods are electrodeposition [12], hydrothermal [13], co-precipitation [14-15], sol-gel [7,16]. Bi-component ZnO-ZnCo₂O₄ (ZnC) and CuO-CuCo₂O₄ (CuC) are synthesized by hydrothermal method [11], Solid state synthesis route [17], electrospinning method [18]. In the present work the bi-component ZnC and CuC are synthesized under microwave assistance method by using pomegranate peel extract as fuel. It is known that the microwaves enhances the reaction rates rapidly by activating the molecules. As a effect of the microwave irradiation, the response time can be reduced to minimum limit. The higher reaction rates with lesser time is the objective of the present work and develop them as the favourable condition for chemical reaction. The *Punica granatum* peels are the biowastes with rich in polyphenols, antioxidants and other bio-molecules which are good at reducing the metal ions. Hence the pomegranate peel extract is the economical and eco-friendly, reducing agent that can favour the spinel formation. If any plant remains are present in the sample, they can be taken away easily by annealing of the sample. Thus the green chemistry plays a great role in simplifying the synthesis techniques and making them better alternatives with respective to cost and eco-friendly.

II. EXPERIMENTAL SECTION

2.1. Materials

Zinc nitrate, copper nitrate, and cobalt nitrate (97% purity) are the precursors, (Merck Chemicals, India) and were used as received for the synthesis without purification. The pomegranate (*Punica granatum*.) fruits were collected from a local fruit market, Madanapalle, Andhrapradesh.

2.2. Preparation of the Plant Extract

The *pomegranate* (*Punica granatum*) peels were cleaned with distilled water, 20g of pomegranate fruit peel was weighed again with distilled water and added in 100 ml of distilled water in 250 ml Erlenmeyer flask and boiled on a gas burner for 15 minutes, cooled and filtered using filter paper, the filtrate thus obtained is used as an aqueous fruit peel extract for synthesis of nanoparticles.

2.3. Synthesis of Metal Cobaltates

The spinel composite nanoparticles are prepared by green chemical routes under microwave assistance using natural reducing and capping agent, the fruit peel extract. The stoichiometric proportion of 1:2, zinc nitrate and cobalt nitrate salts are taken in 50 ml distilled water, that give rise to dark red colour solution. To this solution containing metallic salts, 5 ml of pomegranate peel extract which is green in colour is added and stirred for about 30 minutes using magnetic stirring. The stirring procedure leads to the homogenous mixture of reddish green dark colored solution containing the precursors and this solution is irradiated under the microwave oven for a period of 10 min, with a break at every 60 sec to avoid spilling of the solution. Under microwave irradiation the solution underwent dehydration and decomposition leaving a dark colored residue and it is washed with distal water and ethanol for several times and annealed at 700 °C for 3 hours to obtain the zinc composite ZnO-ZnCo₂O₄ (ZnC). The same procedure is repeated for the formation of copper composite CuO-CuCo₂O₄ (CuC).

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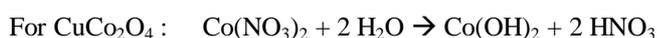
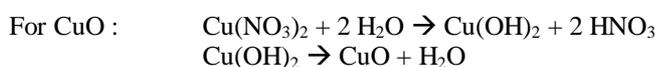
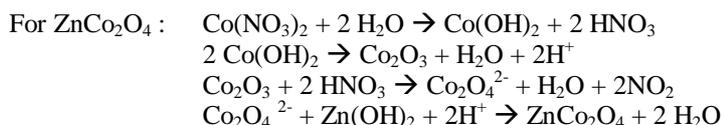
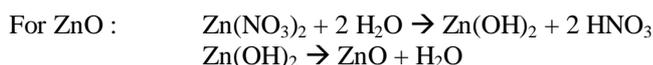
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Scheme.1: Step wise synthesis procedure for the composites.

A schematic representation for the synthesis method is illustrated in scheme-1. From the scheme it is presented, the making of pomegranate peel extract, the metal nitrate solutions, microwave irradiation and annealing. The metal nitrate solutions are mixed respectively, and the peel extract is added to them under stirring. Solutions are irradiated under microwave, the as prepared samples are washed, annealed at 700°C for 3 hours.

The anticipated reaction mechanism for the composite preparation can be described as follows.

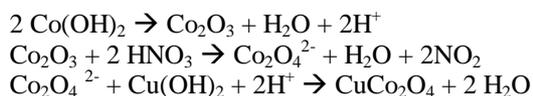


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2.4. Characterization

The PXRD patterns are recorded using Bruker D8 diffractometer for 2θ values ranging from 10 to 80° . The Ziess-SEM instrument for scanning electron microscope (SEM). Jasco FT/IR-4200 infrared spectrophotometer for FT-IR spectra of samples in transmittance mode with wavelength ranging from 400 to 4000 nm. Jasco UV-670 spectrophotometer at room temperature for the optical studies, diffuse reflectance spectra in the wavelength ranging from 200 to 900 nm. Jasco spectro fluorometer FP-6300 at room temperature for the photoluminescence measurements.

III. RESULTS AND DISCUSSION

3.1. Powder X-ray diffraction

The powder XRD pattern for the composites are shown below in figure 1. Figure 1a represents the XRD patterns of sample 'ZnC' (ZnO-ZnCo₂O₄) and Figure 1b represents the XRD patterns of sample 'CuC' (CuO-CuCo₂O₄). From Figure 1a the characteristic peaks of ZnO-ZnCo₂O₄ are observed at 2θ values of 19.13° , 31.40° , 36.97° , 38.66° , 44.92° , 55.76° , 59.45° and 65.33° . These 2θ values can be assigned to (111), (220), (311), (222), (400), (422), (511) and (440) planes of cubic lattice phase of ZnCo₂O₄ with JCPDS card No. 23-1390 (space group Fd3m). The 2θ values at 31.89° , 34.58° , 36.30° , 47.65° , 56.71° , 62.91° , 68.0° and 69.19° corresponds to (100), (002), (101), (102), (110), (103), (112) and (201) planes of ZnO with JCPDS card No. 36-1451 (space group P63mc). Thus conforms the composite formation. Similarly the figure 1b shows the characteristic peaks of CuO-CuCo₂O₄ at 2θ values of 18.89° , 31.16° , 36.74° , 38.71° , 44.69° , 55.55° , 59.26° and 65.15° . These 2θ values can be assigned to (111), (220), (311), (222), (400), (422), (511) and (440) planes of cubic lattice phase of CuCo₂O₄ with JCPDS card No. 23-1390 (space group Fd3m). In figure 1b the 2θ values at 32.59° , 35.63° , 38.80° , 48.85° , 53.53° , 58.37° , 61.63° , 66.31° and 68.17° corresponds to (110), (-111), (111), (-202), (020), (202), (-113), (022) and (113) planes of CuO with JCPDS card No. 41-0254. Thus conforms the formation of composite with two compounds respectively.

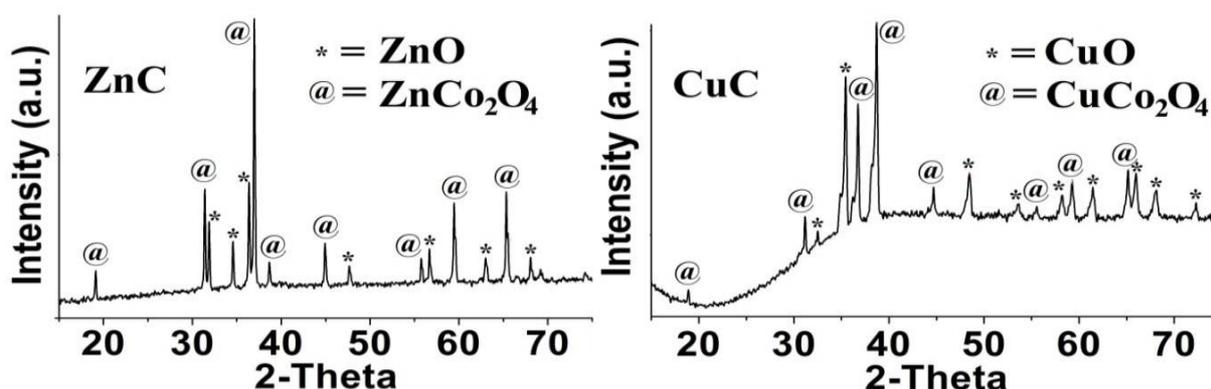


Figure-1: XRD of Zinc Composite (ZnC) (a), Copper composite (CuC) (b).

The peaks and intensities of the synthesized powder and that of the standard shows similar behaviour. This shows the complete formation of composite spinel under the employed experimental condition. The average crystallite size of the samples was calculated using Scherrer formula,

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$$L = \frac{0.94\lambda}{\beta_{1/2} \cos \theta}$$

Where L is the average crystallite size (A°), λ is the X-ray wavelength (0.154 nm), θ is the diffraction angle, and β the peak position and the FWHM (full-width at half maximum) the average crystallite size is found to be 90 ± 2.5 nm for ZnC and 47 ± 2.5 nm for CuC.

3.2 Scanning electron microscopy (SEM) studies:

The scanning electron microscopy is used for studying the surface morphology of the samples ZnC and CuC. The SEM images of bi-component samples ZnC and CuC are shown in figure-2 and figure-3, respectively. The nanoparticles have nearly spherical like structure with various sizes, these small particles are cold welded to form the large agglomerated particles. In both the samples the particle size varies from 0.2 to 0.6 μm . The agglomerated structures are sized in between 1 to 1.5 μm .

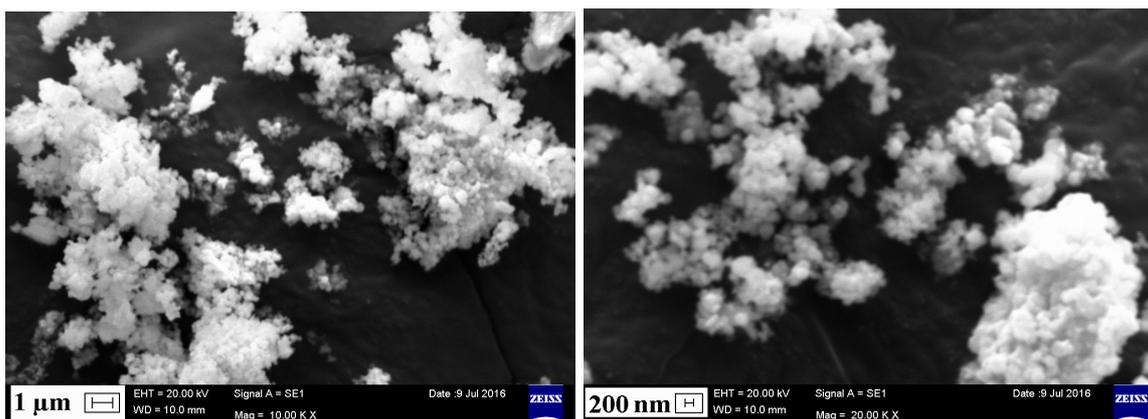


Figure-2: SEM image of Zinc Composite, ZnO-ZnCo₂O₄.

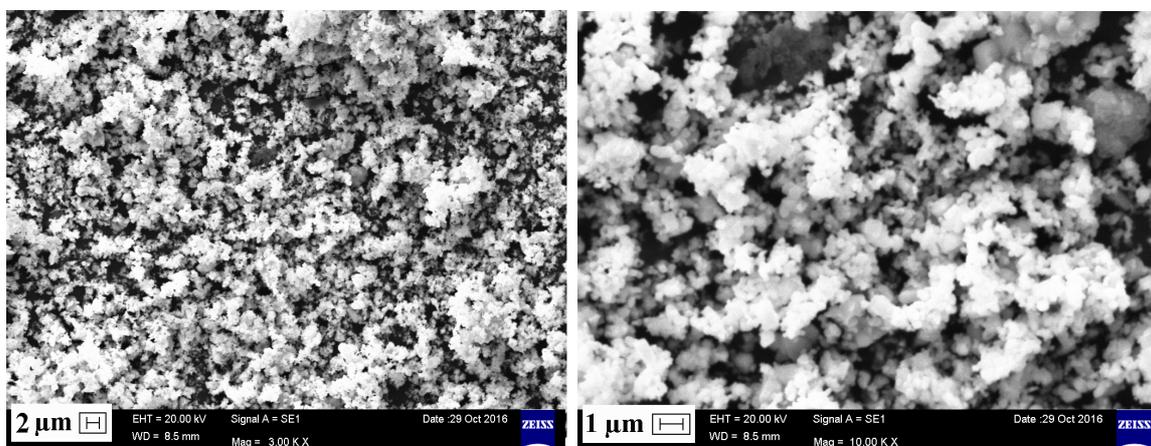


Figure-3: SEM image of Copper Composite, CuO-CuCo₂O₄.

Figure-2 represents the SEM images of samples ZnC, the zinc composite containing ZnO and ZnCo₂O₄. The sizes of the ZnC particles are in good agreement with that of the ZnO-ZnCo₂O₄ synthesised by Junmin Xu et. al. [11]. Junmin

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Xu et. al. synthesised the ZnO-ZnCo₂O₄ by hydrothermal method and the particles are flower like in morphology. Similarly Figure-3 represents the SEM images of samples CuC, the copper composite containing CuO and CuCo₂O₄. The sizes of the CuC particles are in good agreement with that of the CuO-CuCo₂O₄ synthesised by A. Shanmugavani et. al. [19]. A. Shanmugavani et. al. synthesized the CuO-CuCo₂O₄ by the microwave assisted reflux method and the particles are showing the rod like morphology.

3.3. Fourier transform infrared (FT-IR) analysis.

Figure 4 illustrates the FTIR spectrum of respective composite nanoparticles aiming to identify the metallic bond vibrations. The infrared spectra is recorded from 400 – 4000 cm⁻¹ range and is shown for ZnC and CuC in figure 4 (a) and (b) respectively. Both the samples exhibited a common peaks near 3400 cm⁻¹ and 1650 cm⁻¹, which can be attributed to the –OH stretching and bending vibrations. The –OH group may be due to absorption of moisture from the atmosphere during sample preparation. Metal–oxygen, stretching and bending vibrations are absorbed in the frequency range of 400–1000 cm⁻¹.

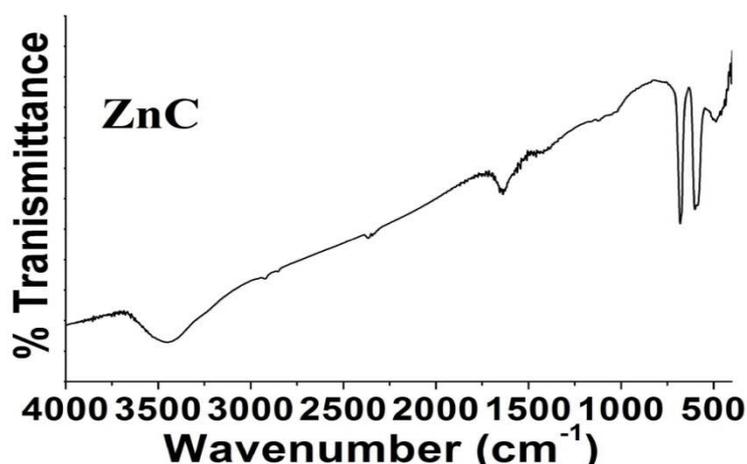


Figure-4(a): FTIR of Zinc Composite, ZnO-ZnCo₂O₄.

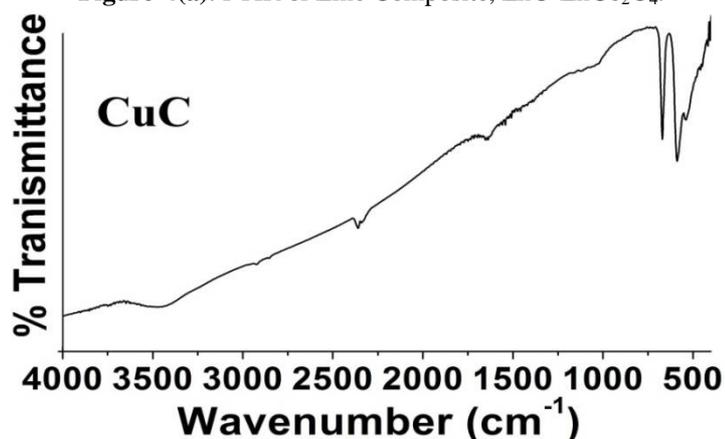


Figure-4(b): FTIR of Copper composite, CuO-CuCo₂O₄.

ZnC nanoparticles in figure 4(a) exhibits the metal–oxygen bond frequencies at 708 and 616 cm⁻¹, which can be attributed to Zn–O–Co, Co–O and Zn–O stretching and bending vibration. From figure 4(b) CuC shows two strong absorption bands at 670.14 and 588.18 cm⁻¹ can be attributed to the Co–O–Cu, Co–O and Cu–O stretching and

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bending vibration. The absorption band at 2400 cm^{-1} in both the samples is originated from the mode of CO_3^{2-} ion. The presence of this CO_2 is may be due to burning of plant material in the process of annealing.

3.4. Optical properties.

The UV-Vis study for the bi-component ZnC and CuC was performed under the Jasco UV-670, a UV-VIS-NIR diffuse reflectance spectrophotometer at room temperature. The spectra recorded are illustrated below in figure-5 and figure-6. The figure-5 represents the absorption spectras of bi-component ZnC and CuC in 5(a) and 5(b) respectively. Zinc and copper cobaltates contains the transition metal and hence exhibit d-d electron transitions, that leads to the UV-absorption. The zinc composite (ZnC) shows UV-absorption bands peaked at 220, 282, and 390 nm respectively. The peaks at 210 can be attributed to the spinel cobaltate and the peaks at 282, and 390 nm are due to the zinc oxide [20] [21]. From figure 5(b), the copper composite (CuC) shows UV-absorption bands peaked at 210, 262, and 410 nm, which represents the copper oxide and cobaltate spinel respectively [21].

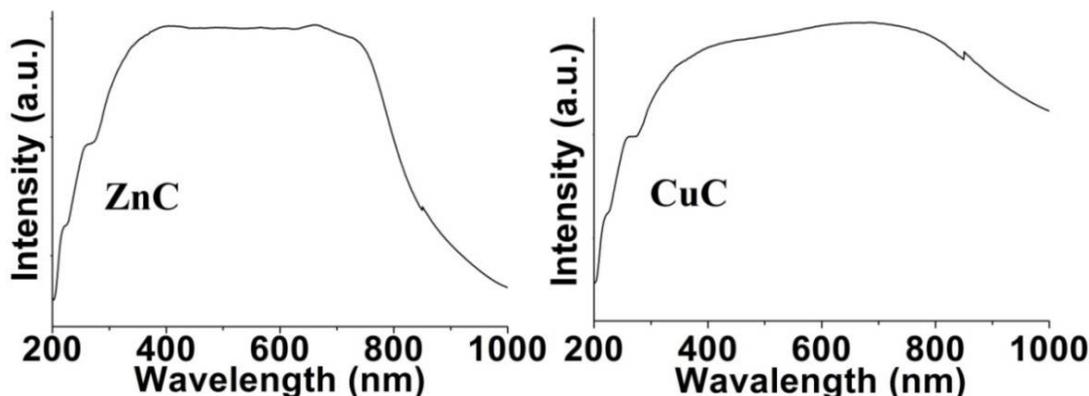


Figure-5: UV-Vis absorbance spectrum of (a) Zinc Composite (ZnC), (b) Copper composite (CuC).

Similarly the figure-6 represents the reflectance spectras of bi-component ZnC and CuC in 6(a) and 6(b) respectively.

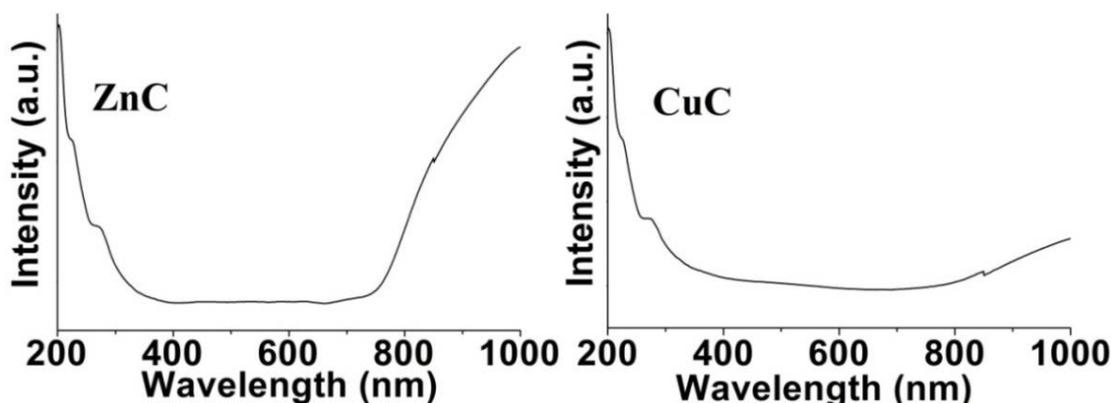


Figure-6: UV-Vis absorbance spectrum (a) Zinc Composite (ZnC), (b) Copper composite (CuC).

The band gap energies for bi-component ZnC and CuC are estimated from that of UV-Vis reflectance spectra and the same band gap energies are represented in figure 7(a) and 7(b) respectively. The optical band gap values for the bi-component Zinc and Cars are estimated by utilizing the next equation:

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$$\alpha(\nu) = A(\hbar\nu/2 - E_g)^{m/2},$$

The band gap is determined by relating diffuse-reflectance (R) of the samples with the Kubelka–Munk function F(R) in the equation $F(R) = (1-R)^2/2R$ and the energy intercept plot of $(F(R)*\hbar\nu)^2$ versus $\hbar\nu$ is plotted, when the linear regions are extrapolated to the zero ordinate, one can get the band gap of the sample.

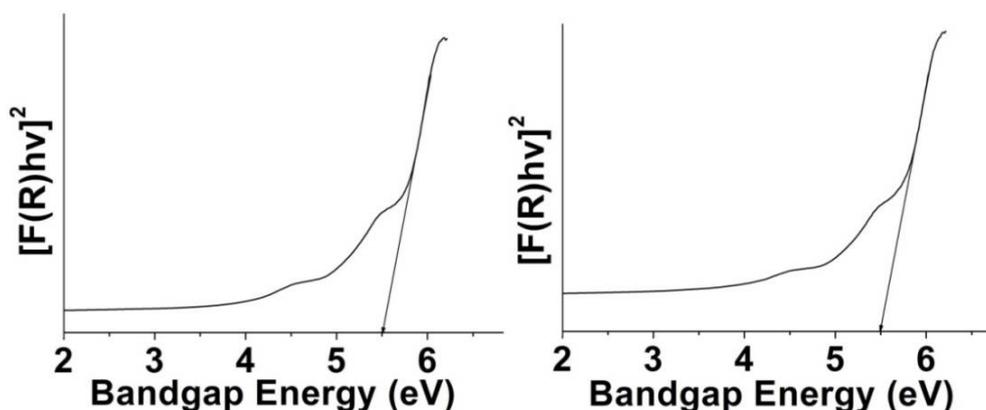


FIG-7: Bandgap energy values for (a) Zinc Composite (ZnC), (b) Copper composite (CuC).

Henceforth, the band gap energy values calculated for bi-component ZnC and CuC samples and are found to be 5.6 and 5.5 eV respectively. The decrease in nanoparticles size leads to the increase in the optical band gap, because of the quantum confinement the decrease in crystal size, band gap energy exhibits an increasing trend. Thus the results from UV–Vis reflectance spectra are in good agreement with that of XRD results.

IV. CONCLUSIONS

In the present work bi-component ZnC and CuC composites are synthesised by biosynthesis method under microwave assistance. In this method the pomegranate peel extract is used as the reducing agent for the reduction of the metal ions into metal oxides or heterometallic oxides. The peel extract is a bio waste and hence it is economical. The role of the natural reducing agent reduces the hazardous effect that caused by the utilization of organic surfactants. Thus, natural reducing agents are cost efficient, harmless, and very effective in the synthesis. The use of a microwave effect in the synthesis enhances the reaction rates by molecular level activation, thus reduces the reaction time. The benefits of natural reducing agent and a microwave effect has made the present work promising for the production of the nanoparticles. The composite of metal cobaltate with metal oxide is successfully synthesized under the present experimental condition. The establishment of the complexes has been supported by the PXRD, SEM and UV–Vis study. Hence the study reveals that the synthesis method employed is effective for the production of bi-component composite nanoparticles.

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