Study of structural features and antibacterial property of ZnO/CuO nanocomposites derived from solution combustion synthesis

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Abstract. ZnO/CuO nanocomposite was synthesized by solution combustion method using three organic fuels - EDTA, Citric Acid and Oxalic Acid with Zinc Nitrate Hexahydrate and Copper Nitrate Trihydrate as precursors. ZnO/CuO nanocomposite was characterised for PXRD, SEM and EDAX to analyse the Structural, Morphological properties and Elemental composition. Crystallite size of 13.82 nm was found for the ZnO/CuO nanocomposites prepared from Oxalic Acid (OA). Further, ZnO/CuO nanocomposites synthesised from three different metal nitrate weight ratios (25:75, 45:55 and 65:35) using OA as fuel and Antibacterial studies was carried out on E.coli by disc diffusion method. PXRD results confirm that the nanocomposites prepared were in nano domain with the average crystallite size was found to be in the range of 13–21 nm. SEM micrographs of ZnO/CuO nanocomposites showed hexagonal ZnO and spherical CuO particles and the particle size was found to be in the range of 30–60 nm. EDAX results confirmed the presence of four elements namely C, O, Cu and Zn. Antibacterial studies showed that the inhibition zone of the nanocomposite was maximum (24 mm for 20 μL) for the sample having high concentration of ZnO nanoparticles and it depends on the crystallite size of the ZnO/CuO nanocomposite.

1. Introduction

Nanocomposites are a blend of different nanomaterials in which at the very least one of the phases exhibit dimensions in the range of nanometre (1 nm = 10⁻⁹ m) [1]. Nanocomposites are of high interest for some innovative applications as they not only just give the best properties of their individual components in them yet additionally make the impressive cooperative energy impacts [2]

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Mixed metal-oxide nanocomposites have found application such as microelectronic circuits, piezoelectric gadgets, energy components, sensors, photocatalysis, and surface covering to avoid consumption, and solar powered batteries [3-5]. Synthesis of nanoparticles based on noble metal and their oxides is being used as a biocidal agent and biotechnology is a field of interest. Recent days, antibacterial property of nano metals and its oxides have found its novel application as a biocidal agent. Also, the majority of researches have proposed that the ions of nano metal oxides, like Copper or Zinc are useful in control of infectious microorganisms in hospitals [6].

Solution combustion is a very effective and efficient technique that can be followed for synthesis of nanomaterials and it is currently being used for preparing variety of complex metal oxide nanopowders for different applications [7-8]. Saravanakkumar D et al [9] have synthesized ZnO-CuO nanocomposites by modified perfume spray pyrolysis technique to investigate antimicrobial property on both gram negative and gram positive bacteria by disc diffusion method. The outcomes of revealed that the maximum Zone of Inhibition (ZOI) against proteus mirabilis of 20 mm for 20 μL. N Widiarti et al [10] have prepared CuO-ZnO composites to study its application as antibacterial agent by sol-gel process. The antibacterial test showed ZnO is highly resistant against E. coli and better at only inhibiting the growth of S. aureus. There was not much difference between the inhibitory property of CuO against both bacteria E.coli and S. aureus. Hence, the blend of CuO-ZnO nanocomposite is used as inhibitors of the bacterial growth of both S. aureus and E. coli.

Mostly used organic fuels in the method of solution combustion are urea-CH\(_2\)\(_2\)N\(_2\)O, glycine - C\(_2\)H\(_2\)N\(_2\)O\(_2\), oxalyl dihydrazide - C\(_2\)H\(_2\)N\(_2\)O\(_2\), carboxyhydrazide - CH\(_2\)N\(_2\)O, EDTA - C\(_{10}\)H\(_{16}\)N\(_8\)O\(_5\), PV alcohol - (C\(_2\)H\(_3\)O\(_2\))\(_2\), PV acetate - (C\(_4\)H\(_8\)O\(_2\))\(_2\), citric acid - C\(_6\)H\(_8\)O\(_7\), sucrose - C\(_{12}\)H\(_{22}\)O\(_{11}\) and dextrose-C\(_6\)H\(_{12}\)O\(_6\). They are divided into two groups one is the nitrogen containing and the other is pure carbohydrates. It is a known fact that a part of the organic fuel can make complexes with the cations of a metal [11, 12]. Since nitrogen does not get involved in the reaction during combustion, it is released as the gaseous product which increases the porosity of the resulting product. The intensity during combustion reaction is proportional to the type of fuel [13]. The fuel’s nature and its quantity, are some of the significant factors involved in a process, for obtaining the porous and foamy product at the end [14]. Thus, the characteristic feature of a fuel is that it must maintain the homogeneity of the compositions and also sustain combustion with the oxidizer at a low temperature of ignition. The characteristics of the powder resulted from the combustion reaction are firstly depended on the temperature of flame produced during the reaction and is a function of the nature of the fuel [15-18].

The ZnO/CuO nanocomposites were synthesised by solution combustion technique. In past decade, the typical methods used to prepare the nanocomposites include hydrothermal method [11], electrochemical method [12], co-precipitation method [13] and sol-gel method [14].

The synthesis of ZnO/CuO nanocomposite by one step solution combustion synthesis (SCS) is reported scarcely. This paper describes the investigation of ZnO/CuO nanocomposite synthesised from different fuels and antibacterial activity of the ZnO/CuO nanocomposites prepared from three different metal nitrate ratios and the effect of crystallite size and quantity of the nanocomposites on bacterial inhibition.

2. Experimental details

2.1. Materials

Every used for preparing ZnO/CuO nanocomposite were of analytical grade and directly used without the purification of any sort. Hydrated zinc nitrate (Zn (NO\(_3\))\(_2\).6H\(_2\)O) and copper nitrate (Cu (NO\(_3\))\(_2\).3H\(_2\)O) is used as a precursor. Three different fuels are used they are Ethylene diamine tetra acetic acid (EDTA - C\(_{10}\)H\(_{16}\)N\(_8\)O\(_5\), citric acid (C\(_6\)H\(_8\)O\(_7\), oxalic acid ((COOH)\(_2\).2H\(_2\)O). The chemicals were dissolved using distilled water. Nutrient agar and Escherichia coli bacteria are used for antibacterial studies.
2.2. Preparation and synthesis of ZnO/CuO nanocomposite

Exactly 10g of metal nitrates (Zn (NO$_3$)$_2$: Cu (NO$_3$)$_2$) were taken in three different ratios (25:75, 45:55, 65:35). The fuel weight was calculated for the 10g of metal nitrate. The calculated amount of precursor and fuel is weighed transferred to a beaker and is dissolved in distilled water to make it a saturated solution. The solution prepared is made sure that the contents are fully dissolved. Then the furnace is preheated to 500°C. The solution is placed inside the preheated furnace at 500°C for 30 min. The resultant product will be ZnO/CuO nanocomposites after the moister content in the solution gets evaporated. The principle of SCS is the effective usage of generated heat during the reaction among oxidizers (metal nitrates) used and the reducing agent (fuel). Here zinc nitrate and copper nitrate are used as oxidisers and three different organic fuels (Ethylene diamine tetra acetic acid (EDTA), citric acid, oxalic acid) as reducing agent. SCS has some specific advantages in the preparation of mixed metal oxide nanoparticles. It can provide high homogeneity of mixed metal nitrates used as a precursor and narrow size distribution, which helps the synthesis of chemically homogenous and well-dispersed hetero junctions with more active contact sites, thereby enhancing the charge transfer efficiency [5-6].

![Figure 1. Solution combustion synthesis process [5]](image)

Fig 1 shows the progress of solution combustion method. The mechanism involved in the reaction is very complicated. The factors which is significant during the reaction are; the type of fuel, fuel-to-oxidizer ratio, quantity of water in the precursor mixture and ignition temperature etc. usually. a good combustion reaction should not be violent, should produce non-toxic gaseous products and acts as a complexant for metal cations [6-8].

2.3. Characterization

The ZnO/CuO nanocomposite was characterized with Powder X-ray Diffraction (PXRD), scanning electron microscope (SEM) and Energy Dispersive Spectroscopy (EDAX).

2.3.1 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction technique is the one of the most basic methods used for characterization of the microstructures of nanocrystals. The typical wavelength of X-rays used in PXRD is around 1Å, which can be compared to inter atomic spacing range of the crystals. The crystallinity and phase identification of powder was investigated using MAXima X XRD-7000 X-ray Diffractometer, in the scanning range (2θ) of 25-70° using Cu Kα radiation having a wavelength of 1.5406Å.
2.3.2 Scanning electron microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS or EDAX)

The SEM is a flexible instrument used for the examination of the microstructure and its analysis. The morphology of the ZnO/CuO nanocomposites were analysed using SEM. EDAX method allows one to recognize a particular element and their relative proportions (at %) in the sample. It is one of the useful techniques that comes integrated with SEM, which allows elemental analysis without destruction of the sample. SEM micrographs were recorded on AMETEK with an integrated EDAX detector.

2.4. Antibacterial property test

The antibacterial performance of the ZnO/CuO nanocomposite was estimated against Gram-negative bacteria E. coli.

2.4.1. Preparation of agar medium and bacterial inoculation

Nutrient Agar is a nutrient medium which can be generally used in the cultivation of microorganisms which supports the growth of a wide range of microbes. Agar medium was prepared by dissolving 4g of Luria broth and 1g of agar in 200ml of distilled water. The solutions were autoclaved along with the petri dish at 121°C for 15 minutes to sterilize the contents. After the autoclave of nutrient agar, agar medium was cooled down to 40-50°C. The agar was poured inside a sterilized glass petri dish to a uniform depth of around 4 mm. The solution in the petri dishes is allowed to solidify. Before using it, the plates are dried in an incubator at 30-37°C, keeping the top partially open, for 30 min or till all of the excess moisture on the surface has been evaporated. Agar medium has to contain moisture but also should be free of water droplets on the surface. Moisture droplets in the petri dish increases the chances of growth of other bacteria, which may present undesirable results. A cotton swab was sterilised and dipped into the standardized suspension of bacteria and the agar is inoculate by spreading it with the swab. Repeat the rubbing by rotating the plate ensure a uniform bacterial suspension distribution. The medium surface was allowed to dry for 3-5 minutes but not more than 15 min which may lead to the absorption of moisture.

2.4.2. Testing for Antibacterial property

ZnO/CuO nanocomposite that needs to be tested was dispersed in a calculated quantity of distilled water, i.e. in the concentration of 200μg ml⁻¹. White discs are used for placing the nanocomposite solution and these discs are placed on the dried plate. After placing the nanocomposites on the disc wrap the petri dishes are covered to make it air tight and incubate the plates in an inverted position in the incubator at 30°C for 24hrs. Observe and record the zone of inhibition produced by each samples after 24hrs.

3. Results and discussions

3.1. X-Ray Diffraction (XRD)

XRD spectrum of ZnO/CuO nanocomposite is shown in Fig 2. ZnO peak (in fig 2a) intensities occur at 2θ values of 36.11°, 31.62° and 34.33° corresponding to the (101), (100) and (002) planes of the hexagonal wurtzite ZnO (JCPDS Card No. 36-1451) phase respectively while those for CuO (JCPDS Card No. 48-1548) occur at 2θ values of 38.63°, 35.39° and 48.56° which can be attributed to (111), (111) and (202) peaks (fig 2b) of the monoclinic CuO respectively. The separation of phase between ZnO and CuO is visible which confirms the presence of both ZnO and CuO in the nanocomposites prepared by three different organic fuels (EDTA (fig 2c), Citric acid (fig 2d) and Oxalic acid (fig 2e)). The diffraction peaks of the ZnO/CuO nanocomposites, pure ZnO and pure CuO are very sharp and intense showing that the high crystallinity. It is seen that CuO stacking prompts increased size of ZnO crystals and the size of ZnO crystals are proportional with increasing
concentration of CuO. Since the ZnO particle size are heavily depended on the concentration of CuO stacking, the density of CuO particle also increases with CuO concentration [21].

**Figure 2.** XRD spectra of ZnO/CuO nanocomposite. (a) Pure ZnO (JCPDS no.36-1451), (b) Pure CuO (JCPDS48-1548), (c) ZnO$_{0.5}$CuO$_{0.5}$/EDTA, (d) ZnO$_{0.5}$CuO$_{0.5}$/Citric acid, and (e) ZnO$_{0.5}$CuO$_{0.5}$/Oxalic acid.

The crystallite size of ZnO/CuO nanocomposites are then estimated from the Equation 1.

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta}$$

Where, D is average particle size, k is the Scherrer constant (0.9), $\lambda$, $\beta$ and $\theta$ are the wavelength of X-ray ($\lambda = 1.5406 \text{ Å}$), the full width at half maximum (FWHM) of the diffraction peak and the Bragg’s diffraction angle, respectively. The average crystallite size of ZnO/CuO nanocomposites prepared from the fuels EDTA, citric acid, and oxalic acid are tabulated in table 1.

**Table 1. Crystallite size of nanocomposites**

| Nanocomposite Samples         | Crystallite size (nm) |
|------------------------------|-----------------------|
| ZnO$_{0.5}$CuO$_{0.5}$/EDTA   | 20.77                 |
| ZnO$_{0.5}$CuO$_{0.5}$/Citric acid | 15.59           |
| ZnO$_{0.5}$CuO$_{0.5}$/Oxalic acid | 14.66            |
| ZnO$_{0.5}$CuO$_{0.5}$/Citric acid | 18.16           |
| ZnO$_{0.5}$CuO$_{0.5}$/Oxalic acid | 13.82            |

The values of crystallite sizes of the nanocomposites prepared from EDTA, Citric acid and Oxalic acid for the metal nitrate ratio of 65:35 are 20.77, 15.59, 14.66nm respectively. Since the crystallite size is smallest for the sample prepared from the oxalic acid is the smallest, it was used as a fuel to prepare 2 more samples of different ratio of metal nitrate (45:55 and 25:75) and the crystallite
size were found to be 18.16 and 13.82nm of metal nitrate ratio 45:55 and 25:75 respectively. The smaller size of the crystallites may be due to the Combustion temperature and the evaluation of large amount of gasses during the synthesis. The XRD graphs of the nanocomposite samples prepared from three different ratios of metal nitrate using Oxalic acid is shown in fig 3.

![XRD spectra of the samples prepared from different metal nitrate ratios using oxalic acid](image)

**Figure 3**. XRD spectra of the samples prepared from different metal nitrate ratios using oxalic acid a) ZnO$_{2.5}$CuO$_{7.5}$, b) ZnO$_{4.5}$CuO$_{5.5}$, c) ZnO$_{6.5}$CuO$_{3.5}$

XRD shows the peaks of ZnO/CuO nanocomposites prepared from three different fuels. The samples synthesised from fuels EDTA (fig 3a) and Citric acid (fig 3b) shows nanometric crystals of size larger than that of Oxalic acid (fig 3c), which is consistent with the values, calculated from XRD patterns. Therefore, the change in the organic fuel used for the synthesis will cause significant effect on the morphology and the yield of the powders obtained [22-28]. According to the investigation by Giahi M [29] the crystallite size of 19 nm was obtained for 10% CuO-ZnO nanocomposite which is similar to the values obtained from the samples prepared using three different fuels.

### 3.2. SEM-EDAX

SEM analysis the ZnO/CuO nanocomposite was analysed which revealed an agglomerated, porous, and sponge like morphologies of the particles and it can also be seen that the nanocomposite mainly consists of hexagonal ZnO particles and the spherical CuO particles. The particle size had a range of 20nm to 80nm. It is observed that the shape as well as particle size are not significantly affected by CuO concentration. SEM micrographs of the synthesised nanocomposite samples with the corresponding EDAX spectra are depicted in fig 4.
Figure 4. SEM micrographs and EDAX graphs of ZnO/CuO nanocomposites synthesised from, a) EDTA, b) Citric acid, c) Oxalic acid.

It can be seen that the agglomeration of particles in all of the prepared samples depicting small spherical CuO particles deposited on the surface of the hexagonal ZnO particles. The agglomeration in case of the sample prepared from oxalic acid (fig 4c) is more compared to the samples of citric acid (fig 4b) and EDTA (fig 4a). EDAX graph confirms the presence of Zn, Cu, O, and C elements. The elemental concentration of Zn and Cu is found to be 60.88 wt%, 24.18wt% in the sample prepared from EDTA fuel (fig 4a), 55.05 wt%, 31.29 wt% in the sample prepared from citric acid (fig 4b), and 57.65 wt%, 23.97 wt% in the sample prepared from oxalic acid (fig 4c) respectively. The presence of ‘C’ element in the spectra of the samples is due to binding different organic compounds to form the composite.

3.3. Antibacterial studies

The bacterial inhibition test was conducted by the method of disc diffusion. The inoculums for the experiment were prepared in a fresh ager broth. Fig 5 shows the initial and final stages of bacterial growth around the nanocomposites of different composition.
Fig 5 shows the images of the zone of inhibition (ZOI) produced by ZnO/CuO nanocomposites at 0hr and 24hrs. Agar solution is poured into a sterilised petri dish and is inoculated by E.coli bacteria. A 200μg/ml concentration of ZnO/CuO nanocomposite dispersed solution is placed on the white discs as shown in fig 5a. The results are observed after 24hrs. It can be seen that the ZnO/CuO nanocomposites were successfully able to inhibit the bacterial growth. The ZOI is measured and recorded. The diameter of ZOI is for the sample ZnO$_{2.5}$CuO$_{7.5}$ (fig 5b), ZnO$_{4.5}$CuO$_{5.5}$ (fig 5b) and ZnO$_{6.5}$CuO$_{3.5}$ (fig 5c) is 10mm, 11mm and 11mm for 10μl quantity and 17mm, 22mm and 24mm for 20μl quantity of ZnO/CuO nanocomposite dispersed solution. Table 2 shows the value of ZOI for different composition of ZnO and CuO [9].

| Nanocomposites | Diameter of ZOI in mm |
|----------------|-----------------------|
|                | For 10ml  | For 20μl |
| ZnO$_{2.5}$CuO$_{7.5}$ | 10        | 17       |
| ZnO$_{4.5}$CuO$_{5.5}$ | 11        | 22       |
| ZnO$_{6.5}$CuO$_{3.5}$ | 11        | 24       |

ZnO/CuO nanocomposites proved effective as an antibacterial agent against the E.coli bacteria. N Widiarti et al [10] performed the antibacterial test which indicated that the ZnO has a very high resistance against E. coli and the inhibition property of CuO was not much better than ZnO against the E. coli. This is the reason that the inhibition zone increases considerably as the composition of ZnO increases in the nanocomposite. The table 2 is represented in a fig 6 to help better understand the performance of the nanocomposites.
The crystallite size of ZnO/CuO nanocomposite of ratio 25:75, 45:55 and 65:35 which are used for the test were 18.038, 15.371 and 14.659 nm respectively. From the bar graph (fig 6) it is seen that as the crystallite size keeps decreasing the zone of inhibition keeps on increasing. The smaller crystallite size shows higher antibacterial performance due to the fact that the Zn$^{2+}$ has a smaller ionic radius (1.39 Å) than that of the Cu$^{2+}$ (1.4 Å) [7]. This indicates that the size has a significant role to play in inhibiting bacteria. The bacterial inhibition performance of ZnO/CuO nanocomposites can be explained as follows.

The larger concentration of the Reactive Oxygen Species (ROS) is majorly related to the smaller crystallite size of the ZnO/CuO nanocomposites, and the reactant molecules diffusivity which can increase the oxygen vacancies. In the present antibacterial research, the antibacterial performance of ZnO/CuO nanocomposites is highly because of the origin of many factors such as reactive oxygen species and Zn$^{2+}$ ion release. After that, the first phenomenon is the formation of Hydrogen Peroxide (H$_2$O$_2$) on the surface of ZnO, where the occurrence of reactive oxygen species such as OH$^-$, H$_2$O$_2$ and O$_2$ is very high. After that the second event follows in which the positive holes are going to split up water (H$_2$O) molecules into H$^+$ and OH$^-$ [8-11]. Then the oxygen molecules dissolved are going to be transformed into radical anions (O$^2^-$) of superoxide, which in turn will react with H$^+$ ions to generate radical ions of HO$_2^-$, that upon frequent bombardment with the electrons will be generating hydrogen peroxide anions (HO$_2^-$). Therefore, HO$_2^-$ anions react with H$^+$ ions that will generate H$_2$O$_2$ molecules. Finally, the H$_2$O$_2$ molecules that are produced, which has the ability to infiltrate the cell membrane and collapses the inter cell system of bacteria and are going to be inhibited [12-14]. The highest antibacterial performance of ZnO/CuO nanocomposite is due to released Cu$^{2+}$ ions which are highly active and can be held responsible for the antibacterial property of the ZnO/CuO nanocomposites.

4. Conclusion

ZnO/CuO nanocomposites were successfully synthesised via one step solution combustion process using three organic fuels (EDTA, citric acid and oxalic acid). The synthesised nanocomposites were characterised by PXRD, SEM and EDX. PXRD results confirm that the nanocomposites prepared were clearly in nanosize with the average particle size were found to be in the range of 13nm to 21nm. Antibacterial test was performed for three different compositions of ZnO and CuO (25:75, 45:55 and 65:35). The crystalline size of these three nanocomposite samples were 18.038, 15.371 and 14.659 nm respectively. It was observed that as the crystalline size keeps decreasing the zone of inhibition keeps on increasing. The smaller crystallite size shows more antibacterial effects because it is well known fact that Zn$^{2+}$ has a lower ionic radius (1.39 Å) than that of the ion Cu$^{2+}$ (1.4 Å).

![Figure 6. Bar graphs representing ZOI formed around ZnO/CuO nanocomposite.](image-url)
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