Synthesis of ZnO and CuO nanoparticles via Sol gel method and Its Characterization by using XRD and FT-IR Analysis

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Research Article

Keywords: CuO and ZnO Nanoparticles, XRD, FT-IR, Sol-Gel Method

Posted Date: January 13th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1234162/v1>

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Abstract

Nanotechnology is a completely unique branch of technology that offers with substances in a very small size between (1-100 nm) with various crystal shapes which include spherical nanoparticles, flower shaped, Nano rods, Nano ribbons, and Nano platelets. Metals have ability to produce large number of oxides. These metal oxides play an major role in many areas of chemistry, physics, material science and food science. In this research, Zinc Oxide (ZnO) and Copper (II) oxide nanoparticles were synthesized via sol-gel process using zinc nitrate and copper (II) nitrate as precursor respectively. The characterization of CuO and ZnO nanoparticles was done by using various techniques. X-ray Diffraction (XRD) indicates the crystallinity and crystal size of CuO and ZnO nanoparticle. Fourier transform infrared spectroscopy (FT-IR) was used to get the infrared spectrum of the sample indicating composition of the sample which contains various functional groups. XRD result shows the particle size of CuO at highest peak 29.4014° was 61.25 nm and the particle size of ZnO at highest peak 36.2476° was 21.82 nm. FT-IR spectra peak at 594.56 cm^{-1} indicated characteristic absorption bands of ZnO nanoparticles and the broad band peak at 3506.9 cm^{-1} can be attributed to the characteristic absorption of O-H group. The analysis of FT-IR spectrum of CuO shows peaks at 602.09, 678.39, and 730.19 cm^{-1} which refer to the formation of CuO. A broad absorption peak noticed at 3308.2 cm^{-1} attributed to O-H stretching of the moisture content.

1. Introduction

Nanotechnology is a completely unique branch of technology that offers with substances in a very small size between (1-100 nm) with various crystal shapes which include spherical nanoparticles, flower shaped, Nano rods, Nano ribbons, Nano platelets. The matchless physical and chemical attributes are end result from its excessive surface-to-volume ratio comparing with micro or nano-sized [1]. The uniqueness of nanoparticles in their physical properties and chemical properties make them subject of great attention. The properties of higher damping in nano particles, their mechanical stability, better thermal conductivity and higher strength are special characters [2]. Metal oxide nanomaterials having excessive surface area have attracted substantial interest for scientific studies because of their applications in the field of optical electronics, sensing devices and nano electronics [3]

There are several methods that have been put forward for synthesis of these materials, namely chemical vapor condensation, arc discharge, hydrogen plasma-metal reaction, and laser pyrolysis with in the vapor phase, The other methods include Sol-gel synthesis, micro-emulsion, microbial processes which occur in liquid state, ball milling which is conducted in solid state[4–5]. The synthesis process of nanoparticles defines largely their properties. The range of metal oxide is great and their range of properties and possible applications appear to be enormous.[6]

Sol-gel process has several advantages. Solitary sol gel installation can yield materials at ultra-temperatures, synthesize nearly any substance, co-synthesize two or more substances with one other, exactly observance the microstructure of the top outputs, and punctually dominance the physical mechanical, and chemical characterizes of the ultimate outputs. [7]

In many literatures, it's far determined that Nano particles of ZnO and CuO gives higher overall performance as compared to that of bulk size [8]. Zinc is a necessary element to our health and ZnO nano particles additionally have right biocompatibility with human cells [9]. Recently ZnO and CuO is listed as safe material by FDA (food and drug administration, (US A) [10,11].

Both copper oxide and zinc oxide have shown varying antibacterial activity in opposition to micro-organism species .They have been utilized in food packaging, wound healing and surface coatings because of their antimicrobial activities. However the anti-microorganism activities of these nano-substances are but to be in comparison against gram positive and gram negative bacteria species [12].

There are several nanomaterials that are applied for numerous food packages on commercial level. Titanium dioxide having a particle size of much less than a hundred nm is widely applied as food added substance and antimicrobial agent for food packaging and potential holders. Silver nanoparticles are applied as antimicrobial agent in food packaging, storage utensils, slicing board and refrigerator and moreover as food supplement. Zinc and Copper oxide are applied as nutritive added materials and moreover as antimicrobial operators in food packaging. [13]

Zinc oxide nanoparticles, which emerge as greater antibacterial as their particle size receives smaller, and chitin, that's a natural substance located with inside the shells of crustaceans like crabs and shrimps. [14]

The aim of this study was to synthesize zinc oxide and copper (II) Oxide of low dimension and analysed the size of particles by using XRD analysis at highest peak and study of various functional group present in synthesized nanoparticles at different peak by using FTIR. After reviewing various protocols [1,3,6-9] for synthesis of nanoparticles This method has novel features, which are of great interest due to its low cost, easy preparation and feasibility. Synthesis of ZnO and CuO nanoparticles by improve sol gel technique is reported by Zinc nitrate as precursor, H_2O_2 (hydrogen peroxide) and calcified at 500^0C for 1 hours & Copper (II) Nitrate as precursor, sodium hydroxide and calcified at $400^0 c$ for 2 hours. Further details are discussed in methodology.

1.1 PROCESSING METHODS:

There are two approaches through which we are able to obtain the synthesis of nano materials. Bottom Up method produces small building blocks which one assembled into large structures. The foremost controlling parameters right here are the crystallinity, morphology, particle size, and chemical composition. Examples: chemical synthesis, laser trapping, self-assembly, colloidal aggregation, etc. The second method is, by "Top Down" method where the large physical compound is transformed into smaller nanostructures. Deposition of film and growth, nano imprint /lithography, etching technology, mechanical polishing etc. are number of the examples. Increase in surface-volume ration causes alternation invarious thermal, mechanical and other properties.[15]

2. Objective Of The Study

A. Synthesis the Zinc Oxide (ZnO) and Cupper (II) Oxide (CuO) nanoparticles by sol-gel method.

B. To study the characteristics of nanoparticles by using XRD diffraction pattern and FTIR Techniques

3. Experimental Section

The chemical reagents used in this experiment were arranged from the commercial sources as guaranteed grade. They were used as received with no further treatment.

a. Synthesis of CuO Nanoparticles:

Chemicals: Copper (II) Nitrate, Sodium Hydroxide pellets, ethanol.

Equipments: Beaker, Magnetic Stirrer, Centrifuge, Dehydrator, muffle furnace, motal & pistol.

Synthesis: The synthesis of CuO nanoparticles via way of means of sol-gel technique was as follow: 4.5 g of copper (II) Nitrate become dissolved in a 100 ml ethanol; 4.5 g of NaOH (Sodium Hydroxide) become dissolved in 200ml ethanol. The solution of sodium hydroxide was added drop wise in the solution copper nitrate with non-stop stirring at room temperatures for 2 hours. Reactions arise and color of sample turns dark blue to black. Let the solution settle down and discard the upper layer. Transfer the gel into Centrifuge tubes and centrifuges at 10,000 rpm for 10 min. Discard the supernatant liquid and wash the sample with distilled water. Repeat the above step 2-3 times. The sample allowed to dry at 80⁰ C until the samples becomes dry then annealed the sample at 400⁰C for 2 hours in muffle furnace, crushed the annealed sample of CuO nanoparticles with Motal and Pistol. Figure 1 shows the Flow Diagram of synthesis of CuO nanoparticles by sol- gel method

b. Synthesis Of ZnO Nanoparticles:

Chemicals: Zinc Nitrate, H₂O₂ (Hydrogen peroxide), Double distilled water, ethanol

Equipments: Beaker, Magnetic Stirrer, Centrifuge, Dehydrator, muffle furnace, motal & pistol.

Synthesis: The synthesis of ZnO nanoparticles via way of means of sol-gel technique was as follow: in this process 15.7 g of zinc Nitrate was added to 500ml of double distilled water with non-stop magnetic stirrer till Zinc Nitrate dissolved completely in distilled water. Then the solution was heated to 50°C and 700 ml of alcohol (ethanol) was added slowly with non-stop stirring. After this, add 6ml of H₂O₂ in drop wise manner to the above solution and mixed it by using a magnetic stirrer until to get a clear solution. Let the solution settle down and discard the upper layer. Transfer the gel into Centrifuge tubes and centrifuges at 10,000 rpm for 5 min. Discard the supernatant liquid and wash the sample with distilled water. Repeat the above step 2-3 times. The sample allowed to dry at 80⁰ C until the samples becomes dry then annealed the sample at 500⁰C for 1 hours in muffle furnace, crushed the annealed sample of CuO nanoparticles with Motal and Pistol. Figure 2 shows the Flow Diagram of synthesis of ZnO nanoparticles by sol- gel method.

Figure 3 indicate the whole process of synthesis of ZnO and CuO nanoparticles by sol-gel process.

3.3 Characterization of ZnO and CuO Nanoparticles: The characterization of synthesized nanoparticles was done by following analytical techniques, such as **Fourier Transform Infrared Spectroscopy (FTIR)**, **X-ray Diffraction (XRD)**.

FT-IR (Fourier Transform Infrared) spectroscopy is a technique which analyses Infrared spectrum of a sample by absorption. The sample may be solid, liquid or in gaseous state. Magnesium oxide nanoparticles show different peaks at different levels in FT-IR measurement, which correspond to different functional groups, and stretches.[16]

XRD (X-ray Diffraction) is used for identification of phase of a sample possessing crystallinity. It also provides information on unit cell dimensions. The homogeneity and bulk composition is ascertained, based on Bragg's law which relates the wavelength of radiation with the diffraction angle and lattice spacing in crystalline sample. [16]

4. Result And Discussion

4.1 X-Ray Diffraction Analysis: The crystal structure and size of CuO and ZnO nanoparticles were analysed by XRD. The sharp peak of Figure 4 and Figure 5 indicates that the nature of nanoparticles was crystalline. X-Ray Diffraction Analysis or X-Ray Crystallography was used to identify the atomic or molecular structure of particles in which the crystalline atoms cause a beam of incident X-rays to diffract in to many specific directions. The crystal structure of CuO and ZnO nanoparticles prepared by sol-gel route has been showed in Figure. (4) and Figure. (5) at CuK α ($\lambda = 1.54056$ A) in the Bragg reflection 2θ range from 10° to 70° and 10° to 80° respectively. Sizes of the crystallite particles were calculated using **Scherrer's equation**.

$$D = K\lambda / \beta \cos\theta$$

Where,

D is the crystallite size of the particles,

Shapefactor is 'K' (0.9 in the present work)

' λ ' is the incident¹ X-ray wavelength (1.54056 A, CuK α),

θ is the diffraction angle and β is the full width half maximum.

From the peak width and intensity the small particle size and better crystallinity of CuO and ZnO can be easily seen in Figure 4 and Figure 5. The higher intensity peaks in XRD pattern of the prepared CuO sample was observed at 2θ - 29.4014, 35.51792, 38.80148, 38.97317 (Figure. 4) and in crystallography, XRD refers to monoclinic shape of CuO crystal as claimed in JCPSD card no. 01-007-2551.) Average particle size of the nanoparticle at highest peak (29.4014°) was determined by using Debye – Scherrer's equation and it was found to be 61.25 nm.

The higher intensity peaks in XRD pattern of the prepared ZnO sample is observed at 2θ - 31.7621, 34.4234, 36.2476 (Figure. 5). XRD pattern of ZnO shows sharp peaks, referring to the crystalline nature. The synthesised ZnO nanoparticles showed a single phase with clear diffraction peaks according to the information provided by reported data (JCPDS card no 36-1451). Average particle size of the ZnO nanoparticles was determined as 21.82 nm at highest peak (36.2476°) according to the Debye – Scherrer’s equation. The crystallinity of ZnO refers to a wurtzite hexagonal structure which is result of penetration of two hexagonal lattices.

XRD analysis data also help to calculate the Elastic strain is. The elastic strain results indicate that if the particle size is less than 20 nm than they have more strain and greater than 20 nm particles have less strain, meaning thereby that the smaller particles have higher strain and bigger particles have lesser strain. These values are in agreement with the literature values [17]. From the Table 1: it was clear that both the CuO and ZnO have less strain

Table 1
Calculated Diffraction angle at highest peak and crystallite size
of CuO and ZnO

Sample	Diffraction angle at highest peak	Average size
CuO	29.4014°	61.25nm
ZnO	36.2476°	21.82nm

4.2 Fourier Transform Infrared Spectroscopy (FT-IR): FT-IR spectroscopy analysis has been done to observe the chemical and structural nature of the particles. The Infrared absorption band identifies the various functional group of the molecule. Both synthesized nanoparticles CuO and ZnO have been scanned from 4000 cm^{-1} to 400cm^{-1} . The region from 4000 to 1500cm^{-1} is functional group region and region from 1500 to 667cm^{-1} is fingerprint region.

The analysis of FTIR spectrum of CuO shows peaks at 602.09 , 678.39 , and 730.19cm^{-1} which refer to the formation of CuO as shown in Figure 6. A broad absorption peak noticed at 3308.2 cm^{-1} attributed to O–H stretching of the moisture content.[18] FTIR measurement of CuO nanoparticles shows different peaks at different levels which corresponds to different functional groups and stretches present in it.

Table 2 indicate the various Absorption peak and their respective Functional group of synthesize CuO Nanoparticles by sol gel Method by using FTIR Spectroscopy

Table 2
Absorption peak and Functional group of synthesize CuO Nanoparticles
calculated by Infrared Spectroscopy Absorption table

(Source: The Libretext Libraries, University of California)

Absorption Peaks (cm^{-1})	Functional Group	Compound Class
602.09266	C-Br Stretching	Halo compound
678.39914	C-Br Stretching	Halo compound
730.199	C=C bending	Alkene
891.50511	C=C bending	Alkene
918.37493	C=C bending	Alkene
1256.19342	C-O stretching	Alkyl aryl ether
1580.35456	N-H Bending	Amine
1811.70041	C=O Stretching	Acid halide
2076.34976	N=C=S stretching	isothiocyanate
2151.21505	$\text{N}\equiv\text{N}\equiv\text{N}$ Stretching	Azide
2157.91075	$\text{N}\equiv\text{N}\equiv\text{N}$ Stretching	Azide
2366.78758	O=C=O Stretching	Carbon Dioxide
2555.24809	S-H Stretching	Thiol
3308.21451	O-H Stretching	Alcohol
3469.76366	O-H stretching	Alcohol

Figure 7. Displays the FTIR spectra of the synthesized ZnO in the range of $4000\text{--}400\text{ cm}^{-1}$. FTIR spectrum of pure ZnO nanoparticles, the peak at 594.56 cm^{-1} was the characteristic absorption of Zn-O bond and the broad band peak at 3506.9 cm^{-1} can be attributed to the characteristic absorption of O-H group. These data are similar to the results observed by others [8]. The peak at 594.56 cm^{-1} is allotted to Zn-O [19].

Various Absorption peak and their respective Functional group of synthesize ZnO Nanoparticles by sol gel method using FTIR Technique shown in Table 3.

Table 3
Absorption peak and Functional group of synthesized ZnO
Nanoparticles calculated by Infrared Spectroscopy
Absorption table (Source: The Libretext Libraries, University
of California)

Absorption Peak (cm^{-1})	Functional Group	Compound Class
507.15511	C-I Stretching	Halo Compound
507.15632	C-I Stretching	Halo Compound
518.82167	C-I Stretching	Halo Compound
531.03456	C-I Stretching	Halo Compound
546.12864	C-I Stretching	Halo Compound
546.81185	C-I Stretching	Halo Compound
553.89901	C-I Stretching	Halo Compound
561.41012	C-I Stretching	Halo Compound
572.56646	C-I Stretching	Halo Compound
594.56307	C-I Stretching	Halo Compound
903.89796	C=C Bending	Alkene
1001.75532	C=C bending	Alkene
1308.83442	C-O Stretching	Aromatic Ester
1416.81481	O-H bending	Alcohol
1585.71691	N-H bending	Amine
3383.91592	O-H Stretching	Alcohol
3506.93442	O-H Stretching	Alcohol

5. Conclusion

Copper oxide and zinc oxide may be synthesized via way of means of the use of sol- gel techniques that have been very natural in generating small sized nanostructures (much less than 100nm). ZnO and CuO nanoparticles had been effectively synthesized via way of means of easy Sol-Gel approach. The organized ZnO nanoparticles have been characterised the use of XRD and FT-IR techniques. The average particle size of CuO and ZnO is calculated as 61.25nm and 21.82nm respectively via way of means of the use of Scherrer's equation of substance dried at 80°C. Elastic Strain of the synthesized CuO and ZnO nanoparticles calculations concluded that the small particles have high strain and large particles have

low strain; each the synthesized nanoparticles size more than 20nm so each particles have low strain. Both synthesized nanoparticles CuO and ZnO had been scanned from 4000 cm^{-1} to 400 cm^{-1} in FT-IR. The evaluation of FTIR spectrum of CuO indicates peaks at 602.09, 678.39, and 730.19 cm^{-1} which consult with the formation of CuO. FTIR spectrum of pure ZnO nanoparticles, the height of peak at 594.56 cm^{-1} changed into the function absorption of Zn-O bond. The CuO and ZnO nanoparticles provide super capability in future packages of food packaging and growing the shelf existence of the product. These Nanoparticles have proven antimicrobial movement, and accordingly, they may be utilized in food packaging medium to save the growth of fundamental food infection microorganisms Also, have application in photocatalysis, gas sensing, biomedical tool and solar display screen packages. The approach has an excessive yield and may be used for big scale synthesis of ZnO and CuO nano particles

Declarations

Acknowledgements: Authors deliver their gratitude to supervisor Prof Sunita Mishra, Dean and Head, School of Home Science for giving proper guidance throught the research, UGC (University Grant Commission) for financial support for the purchase of chemicals and the Babasaheb Bhimrao Ambedkar University, Lucknow for providing all infrastructures to carry out the work and USIC lab for the characterization of nanoparticles.

Funding- UGC [NFOBC] (61-1/2019(SA-III))

Conflict of Interests: The authors declare that there is no conflict of interests regarding the publication of this paper.

Data Availability Statement: The data collected from the respondents are available with the corresponding author and may be provided upon reasonable request.

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Figures

Figure 1

Flow Diagram of synthesis of CuO nanoparticles by sol- gel method

Figure 2

Flow Diagram of synthesis of ZnO nanoparticles by sol- gel method

Figure 3

Pictures of synthesis process of nanoparticles

Figure 4

XRD Pattern of synthesized CuO Nanoparticles

Figure 5

XRD Pattern of synthesized ZnO Nanoparticles.

Figure 6

FTIR Spectroscopy of synthesized CuO Nanoparticles

Figure 7