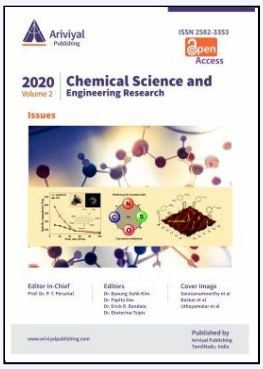
Chemical Science & Engineering Research

Ariviyal Publishing

Research Article

DOI: 10.36686/Ariviyal.CSER.2021.03.06.031

Chem. Sci. Eng. Res., 2021, 3(6), 25-29.



Synthesis and Characterization of Copper Oxide Nanoparticles by Coprecipitation Method: Electronic and Antimicrobial Properties

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ISSN: 2582-3353

Crossref

Publication details
Received: 11th November 2020
Revised: 09th January 2021
Accepted: 18th January 2021
Published: 5th February 2021

Abstract: Monoclinic Copper oxide (CuO) nanoparticles were prepared by simple co-precipitation method. The structural and morphological crystals of CuO nanoparticles were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. To check the bonding between metal and oxide, FTIR was done. In order to study the band gap and optical properties of CuO nanoparticles (NPs), materials were annealed at 200 °C, 300 °C and 400 °C. Upon calcination of CuO nanoparticles at different temperatures, decrease in the band gap from 2.9-2.5 eV was observed. The CuO nanoparticles were also screened for gram positive (Micrococcus letius) and gram negative (E.Coli) bacterial strains. The results revealed that the synthesized CuO NPs could be used as antibacterial agents.

Keywords: Nano materials; XRD; SEM; FTIR; Optical; electronic; antibacterial

1. Introduction

Nano-size materials hold a thousand year history. The silver, gold, palladium and platinum nanoparticles were used in paints by China and Egypt thousands years ago, even without the familiarity of the existence of Nano-materials.[1] Also in medieval period colloidal silver and gold was used for pottery and colouring glass. Up-to the last century there was no logical method that could explain the structure of materials of a size smaller than 1 µm, the information on those materials was restricted. Nanotechnology were developed in beginning of the last century by advancements in the high resolution microscopy methods, Scanning Electron Microscopy (SEM) (1937) and Transmission Electron Microscopy (TEM) (1932) enlightening the scale of 1 nm (10-9m) which is the size of molecules and atoms.[2] With the help of these high resolution microscopic methods one explores the atomic structure and effects of Metal oxide Nano-particles.[3] Due to their high surface to volume ratio and small size, they are having a number of momentous applications in several technological fields, like medical science and industrial sector. Nano-particle research is achieving much more interest due to their unique properties than in bulk like, ductility, improved electrical conductivity, increased strength of alloys and metals, glowing efficiency of semiconductors and formation of ceramics.[4] Here in this case, Cu^{2+} is the oxidation state of Copper in CuO. Its unit cell is having monoclinic symmetry and in the crystallographic unit cell it has four CuO dimers and in the primitive cell it has two CuO units. Each copper atom in CuO is placed in the core of an oxygen parallelogram. In each oxygen atom it has a distorted tetrahedral copper coordination. CuO is a p-type semiconductor and in its ground state it is antiferromagnetic. Due to the optical properties, photothermal, photoconductive applications, magnetic, phase stability properties, high temperature superconducting applications, it has attracted the attention towards exploration and development of CuO nano materials. Experimentally the band gap of CuO has been measured to be 1.2 – 2.0 eV which depends upon the synthesis method and precursor used.

Among the transition metal oxides CuO is one of the most essential nano-particles because of its wide variety of properties. It is a Mott-type insulator due to which its electronic structure cannot be explained by conventional band theory.[5] It acts basis of thermoelectric materials, gas- sensors, high temperature superconductors, magnetic storage media and cosmetics. Besides CuO has good ability in bio-related fields including polluting control, nano-toxicology etc.[6] CuO nanoparticles also have been used as anti-microbial agents.[7-8]

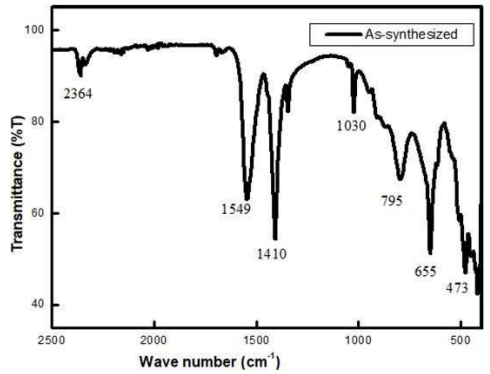

Fig. 1. FTIR spectrum of CuO.

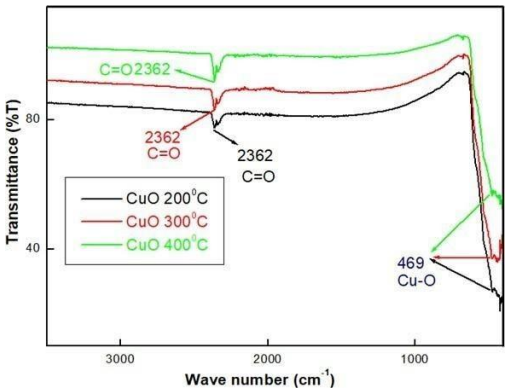

Fig. 2. FTIR spectrum of CuO after calcination at 200 ℃, 300 ℃ and 400 ℃ temperatures.

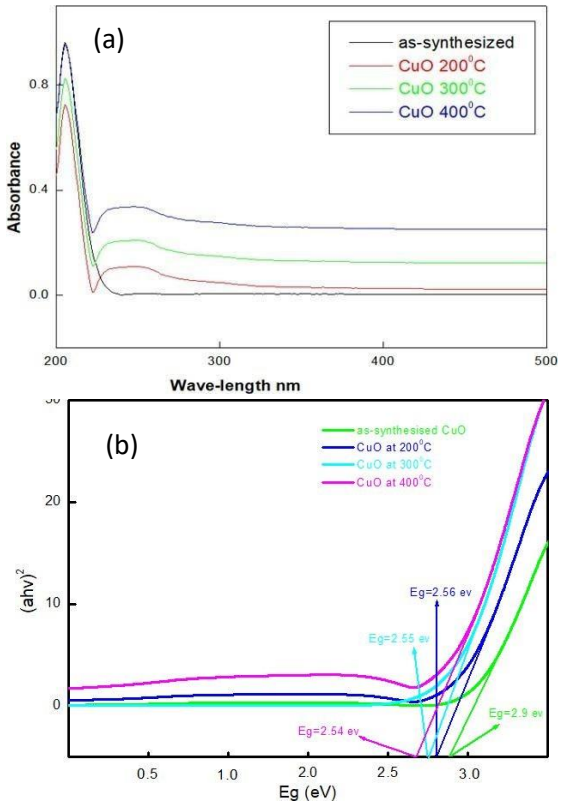

Fig. 3. (a) UV absorption spectrum calcined CuO at 200 ℃, 300 ℃ and 400 ℃ temperatures. (b) UV Indirect-band-gap calcined CuO (200, 300 and 400 ℃).

2. Experimental Section

The Copper acetate Cu $(CH_3COO)_2$ and Ammonia (NH_3) (A.R) were purchased from Sigma Aldrich and were used directly without any further purification for the synthesis of CuO nanoparticles. In this experiment, 19.9650 g of copper-acetate were added to 200 mL of distilled water to make 0.5 M solution and the solution was stirred magnetically for 20 minutes. Ammonia (NH_3) was added drop-wise until colour change occurs (pH change). The above mixture was further stirred for 2 hours till a precipitate was formed.[9] Then the precipitate was washed by distilled water and ethanol and the precipitate was dried to powder form. The powder was annealed at 200 ℃, 300 ℃ and 400 ℃.

3. Results and Discussions

3.1. FTIR analysis

To determine the structural properties (vibrational modes) FTIR of the sample was carried out by FTIR-8400 Shimadzu. The frequency changes were detected in FTIR spectrum due to the interaction between surface molecules and the nanostructures. FTIR spectrum of sample (Fig. 1) shows an absorption bands at 473 cm^{-1} and 655 cm^{-1} which are the characteristic bands of monoclinic phase of Cu-O similar as reported earlier.[10,11] The bands at 1549 cm^{-1}, 1410 cm^{-1} and 1030 cm^{-1} represents the hydro-carbon group (CH, CH_3) impurities which are because of asymmetric stretching, symmetric stretching and out of plane bending.[12] The band at 2364 cm^{-1} confirms the presence of the carbonyl C=O stretching bonds.

The sample was further calcined at 200 ℃, 300 ℃ and 400 ℃ temperatures in order to remove impurities.[13] The Peaks were observed from 464 cm^{-1} to 668 cm^{-1} due to vibrations of Cu-O bond in monoclinic structure of CuO. The absorption peak around 2362 cm^{-1} remain unaffected when temperature was increased from 200 ℃ to 400 ℃ which is because of C=O stretching bond as shown in Fig. 2.

3.2. UV-visible analysis

To study the optical properties of Copper oxide (CuO) nanomaterials, UV-visible spectroscopy was carried out by UV-1800 Shimadzu spectrophotometer and with the help of which band gap was calculated. When the photons of energy greater the band gap is incident to semi-conductor, it absorbs the energy. The electronic LNL/transitions occur from valence band (VB) to conduction band (CB), which in turn shows abrupt increase in the absorbance. The absorption coefficient (α) depends upon the type of electronic transitions.[12] The absorption spectra of synthesized CuO (Fig. 2a) shows that one fundamental absorption edge at 210 nm which is due to the π-π* transition where as for calcined CuO at 200 ℃, 300 ℃ and 400 ℃ absorption edge at 250 nm is observed which is attributed to n-π* transition (Fig. 2b). The band-gap of CuO decreases from 2.9 eV to 2.54 eV on increasing the temperature which is because of reduction in amorphous phase.[14]

$E_g = h\nu = hc/\lambda$

Indirect band-gap = $(\alpha h\nu)^2$: Direct band-gap = $(\alpha h\nu)^{1/2}$

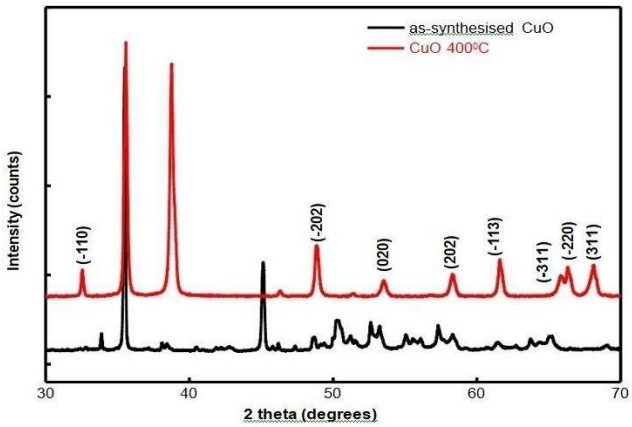

Fig. 4. XRD of as-synthesised and calcined CuO nanoparticles

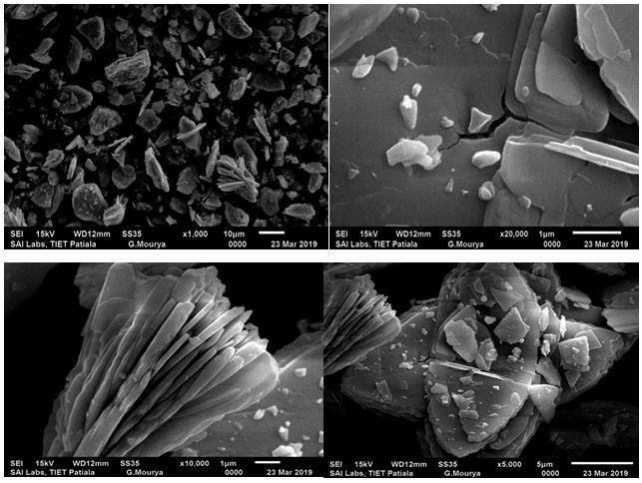

Fig. 5. SEM images of as-synthesized CuO.

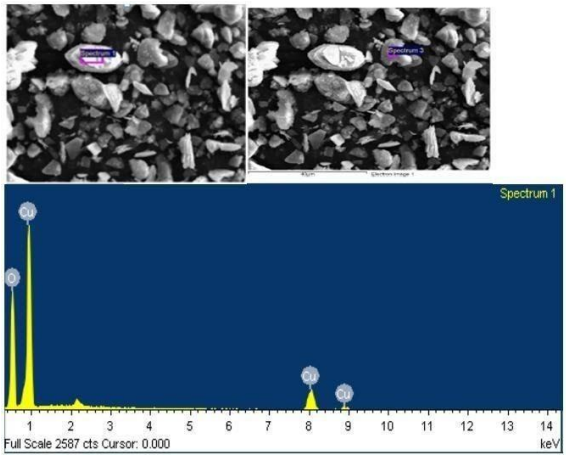

Fig. 6. SEM-EDX spectrum of CuO nano particles.

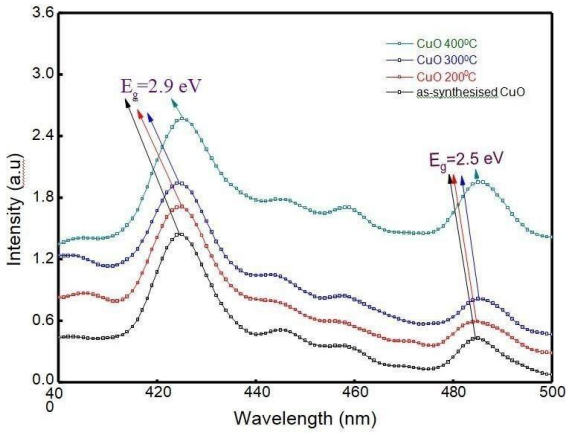

Fig. 7. Photoluminescence spectrum of thin films of CuO calcined at 200, 300 and 400 ℃.

3.3. X-ray Diffraction

The X-ray diffraction analysis was carried out by X-ray diffractometer (XRD, Philips X-Pert) using Ni filtered Cu Kα (λ CuKα = 0.154186 nm, radiation at 40 kv and 30 m). The spectra were recorded from 30 ℃ to 70 ℃ for synthesized and calcined CuO NPs (Fig. 4). The diffraction peaks of CuO NPs were well defined and are in accordance with JCPDS card no. 89-5899, which shows the CuO NPs are having monoclinic structure. The sharp peak from the XRD pattern shows the high crystallinity nature of CuO NPs. The peaks were observed at 32.540, 35.60, 38.70, 48.80, 53.50, 58.30, 61.60, 65.8, 66.30, 680, 72.40, 75.00 and 75.240 which corresponds the (h k l) values of (-1 1 0), (-1 1 1), (1 1 1), (-2 0 2), (0 2 0), (2 0 2), (-1 1 3), (0 2 2), (-3 1 1), (-2 2 0), (3 1 1), (0 0 4) and (-2 2 2) respectively (Table 1).[15,16]

After calcining the sample the average crystallite size was measured 56 nm by using formula:

$$D=0.94\ \lambda/\ \beta \quad (A)$$

Where D is average crystallite size, λ is X-ray wave-length used, β is Full Width at half maximum (FWHM) peak and θ is Bragg's diffraction angle.

Table 1. for position, d-spacing and (h k l) values

S.no	(h k l)	d-spacing	FWHM	2θ(degrees)
1	(-110)	2.74835	0.1748	33.553
2	(-111)	2.52028	0.2498	35.596
3	(-111)	2.32065	0.2613	38.772
4	(-202)	1.86213	0.3074	48.781
5	(020)	1.71054	0.3617	53.529
6	(202)	1.58104	0.3778	58.315
7	(-113)	1.50400	0.3040	61.616
8	(022)	1.41692	0.4815	65.868
9	(-311)	1.4082	0.3731	66.325
10	(-220)	1.3755	0.4473	68.116

3.4. Scanning Electron Microscopy (SEM) and SEM-EDX

The shape and morphology were observed using SEM (JSM-6510, SAI Labs, TIET Patiala). The CuO nano particles were investigated with a magnification of 1 µM, 5 µM and 10 µM which were of different shapes but crystalline in nature as shown in the Fig. 5. From the above SEM images, one could conclude that the synthesized method is one of the suitable ways for synthesizing the pure crystalline copper oxide Nano-particles. By EDX (Fig. 6), it was shown that there was no elemental impurity is present in synthetic material.

Table 2. zone of inhibition

S. No	Bacteria	Sample name	Solvent DMSO concentration (mL)	Sample concentration (mg)	Zone of inhibition (mm)
1	E.Coli	CuO NPs at 200 °C	1 mL	50 mg	8 mm
2	E.Coli	CuO NPs at 200 °C	1 mL	25 mg	5 mm
3	E.Coli	CuO NPs at 200 °C	1 mL	15 mg	0.5 mm
4	E.Coli	CuO NPs at 200 °C	1 mL	10 mg	0 mm
5	Micrococcus Lutes	CuO NPs at 200 °C	1 mL	50 mg	5 mm
6	Micrococcus Lutes	CuO NPs at 200 °C	1 mL	25 mg	3.5 mm
7	Micrococcus Lutes	CuO NPs at 200 °C	1 mL	15 mg	0 mm
8	MicrococcusLutes	CuO NPs at 200 °C	1 mL	10 mg	0 mm

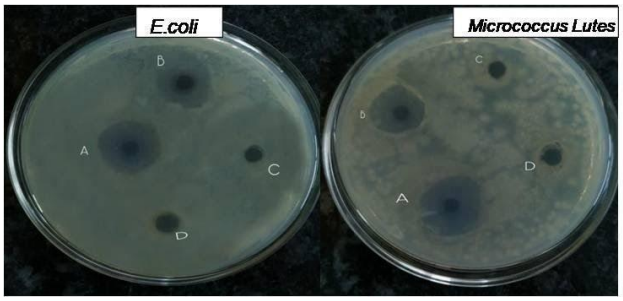

Fig. 8. Antibacterial activity of CuO nanoparticles against E.Coli and Micrococcus Luteus: (A = 50 mg/ mL, B = 25 mg/mL, C = 15 mg/mL and D = 10 mg/mL)

3.5. Photoluminescence (PL)

Photoluminescence investigation of CuO NPs (Fig. 7) showed two main peaks in the visible light band at 430 nm and 488 nm, the band gap energy was estimated to be 2.9 eV and 2.5 eV respectively. This result is in agreement with the band-gap of CuO nanoparticles prepared using a microwave irradiation process. With the increase in calcined temperature, Photoluminescence intensity was increased which is due to the decrease in dislocation density.[17] The two main PL emission bands at 430 nm and 488 nm in the visible range of CuO Nanoparticles. This may be attributed to the surface defects, interstitials and oxygen vacancy arising from the oxygen deficiency and Cu interstitials.[18]

3.6. Antibacterial activity

The antibacterial activity of CuO NPs was tested against the selected E.Coli (Gram negative) and Micrococcus Leutes (Gram positive) bacterial strains cultured in Agar agar medium (type 1GR666-500g, Himedia) are as shown in Fig. 8. The result in the tabulated form (Table 2) shows increase in the antibacterial activity with the increase in concentration of CuO NPs.

The zone of inhibition of E.Coli revealed the highest sensitivity toward CuO NPs while Micrococcus Leutes revealed the least sensitivity. The difference in the activity against these two types of bacteria could be attributed to the structural and compositional differences of the cell membrane. This difference could also be due to the difference in cell wall composition of two bacteria. Gram positive (Micrococcus Leutes) bacteria is having thicker layer of peptidoglycan than Gram negative (E.Coli) which may allow the CuO nanoparticles to interact and hence interrupt the cell functions. So it was unbreakable for CuO-NPs to penetrate it in case of Micrococcus Leutes and led to a low antibacterial effect. That is why the CuO nanoparticles are highly effective against E Coli than Micrococcus Luteus.[19] Various mechanisms have been recommended to explain the antibacterial activity of nanomaterials, such as the production of physical damage and release of metal ions. Physical damage is an efficient mechanism in the inhabitation of bacterial growth.[20-22]

4. Conclusions

Copper oxide nanoparticles were synthesized by co-precipitation method. The material was characterized by XRD, SEM, UV-Visible and FTIR. XRD confirms the monoclinic crystalline phase of copper oxide nanoparticles with particle size around 56 nm. SEM studies showed that the particles are of different shapes and various sizes. The band gap of copper oxide nanoparticles was found to decrease from 2.9 eV to 2.5 eV upon increase of calcined temperature. Photoluminescence spectra showed that the intensity of emission and emission peak wavelength changes with the increasing the calcined temperature. The antibacterial activity of copper oxide nanoparticles over Gram positive and Gram negative was effectively done which showed that copper oxide nanoparticles possess antibacterial property.

Acknowledgements

Asif Ahmad Bhat highly acknowledges the Institute (Lovely Professional University Phagwara) for research facility, and department of chemistry, Govt Model Degree College Shopian for their support and discussions throughout their work. M. A. Kaloo gratefully acknowledges Department of Science and Technology, New Delhi for INSPIRE-FACULTY research grants [DST/ INSPIRE/04/2016/000098].

Conflicts of Interest

The authors declare no conflict of interest.

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