

Exploring the optical and biological aspects of sodium- doped CuO nanoparticles

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HIGHLIGHTS

- Undoped and Na-doped CuO nano-powders were synthesized by coprecipitation method.
- XRD, FESEM and HRTEM were used to analyse the structural properties and surface morphology of the nano-powders.
- The influence of Na doping on the optical parameters of the nano-powders was investigated.
- The antibacterial activity of the nano-powders was tested against Gram-negative and Gram-positive bacteria.
- The highest antifungal activity was achieved against *Candida albicans*.

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ABSTRACT

In this article, we present a novel coprecipitation technique for synthesizing pure and sodium-doped CuO ($\text{Cu}_{1-x}\text{Na}_x\text{O}$) nano powders with different sodium concentrations ($x = 0, 0.01, 0.02, 0.04, 0.06, 0.08, \text{ and } 0.10$). The structural properties of the samples were analysed using powder X-ray diffraction (PXRD), which revealed an average crystallite size of 12.48–10.50 nm. The bonding nature of the $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples was described by Fourier transform infrared (FTIR) spectroscopy. The UV–Visible spectroscopic analysis showed a band gap energy of 1.240–1.456 eV and a refractive index that decreased with an increase in Na doping concentration. Field emission scanning electron microscopy images revealed the spherical, flower-shaped, and flake-like morphologies of the nanoparticles, which had sizes ranging from 42.45 ± 5.49 – 33.98 ± 4.32 nm. Energy-dispersive X-ray spectroscopy and elemental mapping were used to confirm the purity of the samples and the presence of Cu, O, and Na elements in the $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples. High-resolution transmission electron microscopy photomicrographs confirmed that the samples were polycrystalline and the nanoparticles exhibited nucleation with lattice spacing, as shown by selected-area electron diffraction patterns. Furthermore, the $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano powders exhibited efficient antibacterial and antifungal activities. The antibacterial activity was tested against major bacterial strains, and the highest inhibition zones were observed to be 13.67 ± 1.11 mm ($x = 0.06$), 10.67 ± 0.94 mm ($x = 0.10$), 15 ± 1.11 mm ($x = 0.10$), and 9.25 ± 0.25 mm ($x = 0.06$) for *P. aeruginosa*, *B. subtilis*, *S. aureus*, and *K. pneumonia*, respectively. In addition, the antifungal activity of the Na-doped CuO nano powders was found to be enhanced against polymorphic fungus *C. albicans* and filamentous fungus *A. niger* with dopant concentration. These results suggest that Na-doped CuO NPs have potential applications in formulating new antifungal drugs and treating various life-threatening bacterial infections.

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1. Introduction

In the recent past the research on nanomaterials has drastically increased due to various features such as their unique chemical and physical properties [1]. Nanostructures are having dimensions in the nanoscale range and possess excellent efficiency towards bio-medicinal activity of various pathogens because of their high chemical steadiness, small particle size, and large surface to volume (S/V) ratio.

Particularly metal oxide nanoparticles (NPs) have gained sufficient interest due to their wide range of applications in solar cells, sunscreens, gas sensors, cosmetics, oxygen pumps, diesel fuels, and bottle coatings to block ultraviolet radiation [2–4]. Copper oxide (CuO) nanoparticles are among one of the most extensively attracted transition metal oxides because of their biomedical, antimicrobial, anticancer, antioxidant, and biocide applications [5,6]. CuO is a p-type semiconductor with optical band gap of 1.2 eV having unique photocatalytic, photovoltaic, magnetic, and electrical properties [7]. These nanoparticles have been used for different applications such as lithium-ion batteries, near-infrared filters, super-capacitors, catalysis, spintronics, magnetic storage media, and nanofluids [8,9].

The fabricated CuO nanoparticles as reported in the literature have different morphologies, such as needle-like, cauliflower-like, shuttle-like, microspheres, rhombic crystal strips, ellipsoidal, sinter-like, rice-like, rod-like [10–14] etc.

Further, the substitution of metal ions into CuO may affect the electrical, magnetic, and optical properties due to the modification of its electronic structure. Several researchers have reported the fabrication of successful doping or co-doping with transition/rare earth metals including Co [15], Tb [16], Mg, Zn, Ce [17], Ag [18], Ni [19], Fe [20], Mn [21], Mn/Co [22], La/Ni [23], and Fe/Co [24]. S. Janet Priscilla et al. reported the synthesis and characterization of sodium doped CuO NPs [25] and in another study, Hafsa Siddiqui et al. has reported the structural, optical, and electrical properties of Na-doped CuO nanostructures [26], but still found limited research reported on Na-doped CuO nanoparticles. Interestingly, sodium, an alkali metal, plays an excellent role in the growth process of various metal oxide nanoparticles and observed the improved results in different application [27]. However, the detailed scientific investigation is still incomplete on optical, catalytic, structural, biological, and antimicrobial characterization of sodium-incorporated CuO NPs. Therefore, we reported in this work, the successful incorporate of sodium ions into CuO crystal lattice and rigorously studied the optical, structural, catalytic, morphological, antibacterial, and antifungal properties.

Pure and doped CuO nanostructures have been prepared by various chemical and physical methods available such as sol-gel route [28], Sonochemical technique [29,30], hydrothermal [31], electrodeposition process [32], precipitation-pyrolysis method [33], ball-milling [34], microwave irradiation method [35], colloidal thermal [36], solid-state reaction technique [37], chemical vapor deposition [38], co-precipitation process [39], and thermal decomposition method [40], etc. Facile co-precipitation route is most accessible and one of the simplest methods for preparing the metal oxide (MO) nanoparticles [39]. The co-precipitation method is advantageous over others as this process allows us to obtain desired nanomaterials with high degree of crystallinity, excellent homogeneity of nucleation, high purity, small size with definite morphology, and possibility to create homogenous precipitation and it requires minimal energy, lower reaction time and moderate temperature.

The sensitivity towards antimicrobial activity have become significant problem in healthcare and biomedical areas due to increasing various alarming pandemics attack these days. The treatment of these bacterial diseases and fungal infections have been studied using nanotechnology as a potential alternative to the present traditional antibiotics, which have certain restrictions associated to toxicity and exposure time [41,42]. The nanotechnology proposes appropriate solution to overcome such problems with the use of various nanomaterials that

have a broad spectrum of size distributions, high surface to volume ratio, elemental compositions, surface charges, biocompatibility, greater surface to volume ratio, morphologies, and unique surface modification properties [43,44]. Specifically, doped metal oxide nanoparticles with tunable physicochemical properties and biological features such as superior antibacterial, and antifungal potentials, were attractive to be used as efficient antimicrobial tools to eradicate microbial infections [45–47]. However, still there is need to overcome a series of challenges with respect to better understanding of toxicity, process quality, bio-distribution, and long-term effect of chemically synthesized nanomaterials to achieve accurate clinical translation.

In present study, an attempt has been made to prepare undoped and sodium doped CuO ($\text{Cu}_{1-x}\text{Na}_x\text{O}$) nano-powders by co-precipitation method. The synthesized nano-size powders were characterized by using PXRD, FTIR, UV-Visible, FESEM, EDS, HRTEM and SAED analyses. In addition, the obtained samples were screened for antibacterial activity studies by employing Gram(-ve) bacterial cultures *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, and Gram(+ve) bacteria *Bacillus subtilis*, *Staphylococcus aureus* using Disc diffusion method. Furthermore, the antifungal activities of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders were evaluated against two fungal species *Aspergillus niger* and *Candida albicans*.

2. Experimental section

2.1. Chemicals used

Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) ($\geq 98.00\%$), Deionized water ($\geq 99.58\%$), Sodium Hydroxide Pellets (NaOH) ($\geq 97.00\%$), and Sodium acetate anhydrous LR (CH_3COONa) ($\geq 99.00\%$) were used. All the materials are used without further purification. The materials used for the synthesis were listed in Table 1.

2.2. Synthesis of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders

The pure copper oxide (CuO) nano-powders have been prepared by using the simplest facile co-precipitation approach. In the process, Copper(II) sulfate pentahydrate and sodium acetate were used as starting materials. For the synthesis of pure CuO, 24.96 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is dissolved in 100 ml of distilled water and continuously stirred it for 1 h. Similarly, 4 g of NaOH pellet is dissolved using 100 ml of distilled water in a separate glass beaker and constantly stirred for 1 h. Thereafter, the NaOH solution is slowly added dropwise to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution at constant stirring rate for 3 h at 65°C and as a result, precipitate solution was formed. This black precipitate solution is then centrifuged and washed many times repeatedly with ethanol and distilled water until the pH equals to 7. The solid precipitate precursor was dried at 90°C in a hot air oven for 12 h and grinded using piston mortar. Subsequently, the dried samples are annealed at 450°C in a muffle furnace at a heating rate of $2^\circ\text{C}/\text{min}$ for 3 h to obtain nano-sized pure CuO powders. The procedure involved in this approach is as follows:

Table 1

List of chemicals used with their purity and source used for synthesis of Na^+ doped CuO ($\text{Cu}_{1-x}\text{Na}_x\text{O}$) powders.

Precursor	Chemical formula	Molecular Weight (g/mol)	Purity (%)	Source
Copper(II) sulfate pentahydrate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	249.68	98.0–102.0	Merck Specialities Private Limited
Sodium acetate anhydrous LR	CH_3COONa	82.03	99.0	Molychem
Sodium Hydroxide Pellets	NaOH	40.00	97.0	Qualigens

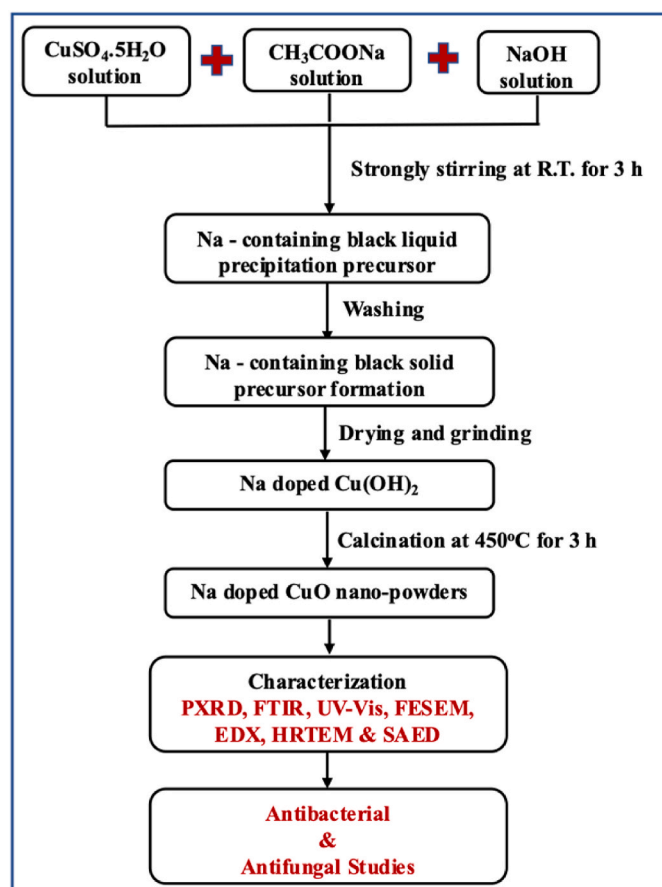
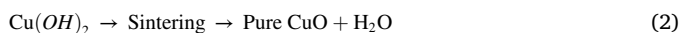
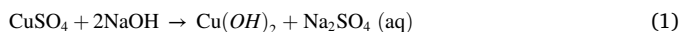


Fig. 1. The flow chart of sodium doped Copper oxide ($\text{Cu}_{1-x}\text{Na}_x\text{O}$) nano-powders synthesized by the Co-precipitation method.



For the synthesis of sodium doped copper(II) oxide nano-powders ($\text{Cu}_{1-x}\text{Na}_x\text{O}$), the stoichiometric aliquots of solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Sodium acetate (CH_3COONa) and NaOH have been prepared in

individual glass beakers and utilized as starting precursor solutions. For $\text{Cu}_{1-x}\text{Na}_x\text{O}$ ($x = 0, 0.01, 0.02, 0.04, 0.06, 0.08$ and 0.10), the same preparation procedure was followed as shown in Fig. 1. CH_3COONa solution was adjoined completely into the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution by maintaining constant magnetic stirring at 65°C for 3 h followed by the slow drop-wise addition of NaOH solution, resulted in the formation of homogeneous bluish mixture solution. The bluish coloured solution is then changed to a dark greenish coloured solution. This mixture solution has now undergone centrifuging and cleansing several times with ethanol and deionized water (1:1). Thereafter, the solid precursor was dehydrated at 90°C in a vacuum oven for almost 12 h to eliminate moisture. Succeeding, the dehydrated sample was kept in a muffle furnace at 450°C for 3 h to get a black coloured sodium doped CuO nano-powders and the obtained products kept for further characterizations.

2.3. Characterization

The powder X-ray Diffraction (PXRD) analysis was performed by PANalytical X'Pert PRO powder X-ray diffractometer using $\text{Cu K}\alpha$ radiation in 20° to 80° range at normal temperature. The Fourier Transform Infra-Red (FT-IR) analysis was carried by using Thermo Nicolet 380 FTIR spectrophotometer in the wavenumber range of 4000 cm^{-1} – 500 cm^{-1} . The UV-Visible absorption analysis was executed in the wavelength range of 200–800 nm by UV-DRS-spectrophotometer, Thermofisher Evaluation 220. With the help of Field Emission Scanning Electron Microscope SIGMA™ FESEM (CARL ZEISS NTS Ltd), the field emission scanning electron microscopy (FESEM) analysis was studied. Energy Dispersive X-ray Spectrometer Quantax 200 with X Flash® 6130 performed the Energy Dispersive X-ray Spectroscopy and elemental mapping studies. The High-Resolution Transmission Electron Microscopy (HRTEM) study was performed by JEOL-2100+ High-Resolution Transmission Electron Microscope.

2.4. Antimicrobial activity test

Copper oxide nanoparticles (CuO-NPs) exhibit the strong antimicrobial activity against selective bacteria and fungi and they can be used as dynamic anti-bacterial agents as well as promising antifungal agents due to their high surface morphology [48]. The antimicrobial activity studies of the pure and Na doped CuO (1, 2, 4, 6, 8 & 10%) nano-powders were performed against four bacterial strains and two

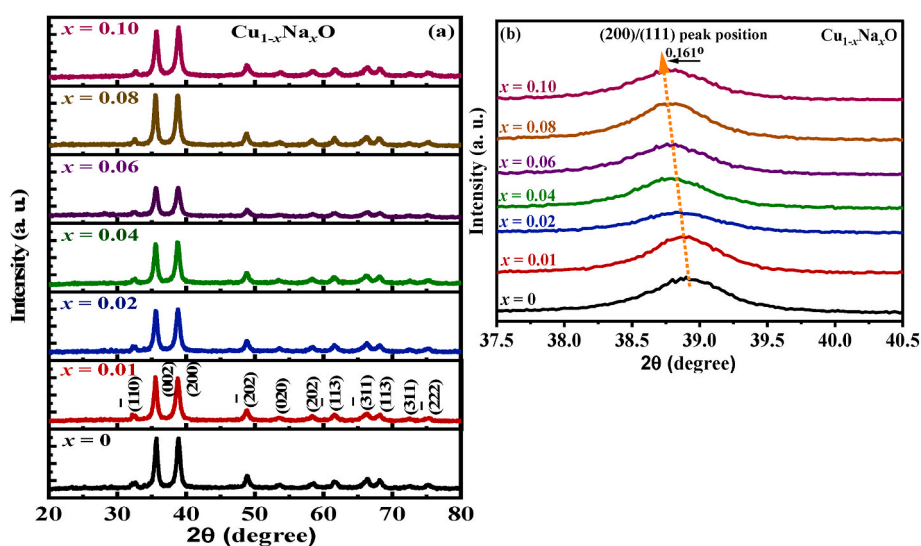


Fig. 2. (a) Comparison of powder x-ray diffraction (XRD) patterns of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples calcined at 450°C for 3 h; and (b) Shift of the (200)/(111) peak towards the low diffraction angle.

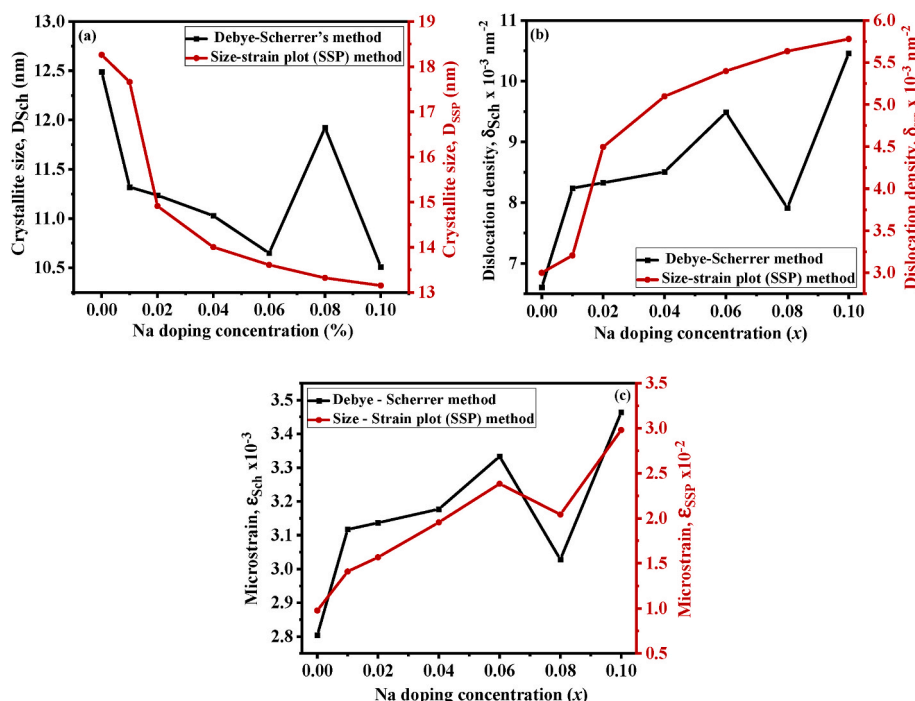


Fig. 3. Comparison (a) crystallite size between average Debye-Scherrer's (D_{Sch}) and Size-Strain plot (SSP) method (D_{SSP}), (b) dislocation density between average Debye-Scherrer's ($\delta_{avg.}$) and Size-Strain plot (SSP) method (δ_{SSP}), and (c) lattice strain among average Debye-Scherrer's (ϵ_{Sch}) and Size-Strain plot (SSP) method (ϵ_{SSP}) of $Cu_{1-x}Na_xO$ nano-powders.

Table 2

The average values of crystallite size (D), dislocation density (δ), lattice strain (ϵ), X-ray density (ρ_{X-ray}), unit cell volume (v), and crystallite volume (V) of $Cu_{1-x}Na_xO$ nano-powders, calculated according to Scherrer method.

Na ⁺ content (x)	D (nm)	$\delta \times 10^{-3}$ (nm ⁻²)	$\epsilon \times 10^{-3}$	ρ_{X-ray} (g/cm ³)	v (Å ³)	V (nm ³)
0	12.4874	6.6059	2.8040	6.5535	80.6210	1947.2390
0.01	11.3187	8.2367	3.1172	6.4915	80.9765	1450.0828
0.02	11.2367	8.3287	3.1371	6.4655	80.8848	1418.8004
0.04	11.0286	8.5061	3.1775	6.3819	81.1002	1341.3926
0.06	10.6491	9.4876	3.3332	6.3343	80.8591	1207.6443
0.08	11.9222	7.9139	3.0284	6.2283	81.3704	1694.6173
0.10	10.5095	10.4578	3.4639	6.2091	80.7544	1160.7713

Table 3

The calculated values of monoclinic unit cell parameters (a , b , c , and β) of $Cu_{1-x}Na_xO$ samples.

Na ⁺ content (x)	Lattice constants			Inter-axial angles		
	a (Å)	b (Å)	c (Å)	α (deg.)	γ (deg.)	β (deg.)
0	4.6922	3.4167	5.1025	90	90	99.432
0.01	4.7044	3.4207	5.1167	90	90	99.445
0.02	4.7048	3.4178	5.1121	90	90	99.562
0.04	4.7033	3.4204	5.1148	90	90	99.443
0.06	4.6969	3.4145	5.1072	90	90	99.419
0.08	4.7081	3.4265	5.1160	90	90	99.515
0.10	4.6925	3.4102	5.1004	90	90	99.512

fungus pathogens. The regular bacterial strains of *Pseudomonas aeruginosa* (Gram negative, MTCC ID - 424), *Staphylococcus aureus* (Gram positive, MTCC ID - 1430), *Klebsiella pneumoniae* (Gram negative, MTCC ID - 39), and *Bacillus subtilis* (Gram positive, MTCC ID - 441); while *Aspergillus niger* (MTCC ID - 281) and *Candida albicans* (MTCC ID - 183) fungi species were selected for this study. These bacterial and fungal strains were procured from the Microbial Type Culture Collection and

Gene Bank (MTCC), Council of Scientific and Industrial Research (CSIR) - Institute of Microbial Technology (IMTECH), Sector - 39A, Chandigarh - 160036, India. The antimicrobial activities of $Cu_{1-x}Na_xO$ samples were employed by the well-established Kirby-Bauer disk diffusion technique on potato dextrose agar media (for fungal strains) and nutrient agar media (for bacterial strains) and disc plates [49].

The disk diffusion test by the Kirby-Bauer process [50] was screened to evaluate the observed antimicrobial activities of sodium-doped CuO nanopowders. The potato dextrose agar (PDA) media and nutrient agar media used for the antifungal and antibacterial activities were sterilized by the application of autoclave at 15 lbs pressure and 121 °C temperature for 15–20 min. To solidify the molten agar, the agar solution is poured into sterile circular glass Petri dishes. Then various fungi and bacteria were cultured separately 24 h in a broth and selected fungal and bacterial strains were uniformly introduced on a solidified dextrose agar media and nutrient agar in a glass Petri plates, respectively. Simultaneously, the Whatman filter paper disks of about 6 mm were individually coated with Na-doped CuO at the graded concentrations of 0 mg/ml, 10 mg/ml, 20 mg/ml, and 30 mg/ml and carefully introduced on the culture. Moreover, the 0 mg/ml concentration was considered to be the control in the experiment. The plates with bacterial cultures were kept for incubation at 37 °C for 24 h and the agar plates having fungal strains were kept for incubation at 24 °C for 48 h, respectively [51]. All the antimicrobial applications were performed in a sterile laminar flow cabinet. The obvious inhibition zones observed around the well were measured, which shows the antimicrobial activity.

When Na⁺ ions are incorporated into the CuO host, with an increase in doping concentration of Na⁺, the antimicrobial activity of Na-doped CuO NPs will be studied against selected pathogenic microorganisms including bacteria, and fungi in terms of zone of inhibition [8]. The zone of inhibition (ZoI) is the circular area observed around the antibiotic NPs on the disc where the microorganisms are unable to grow. The average value of zone of inhibition of as-prepared samples is measured using a ruler and is expressed as mean value $\pm$ SD in millimetres [10].

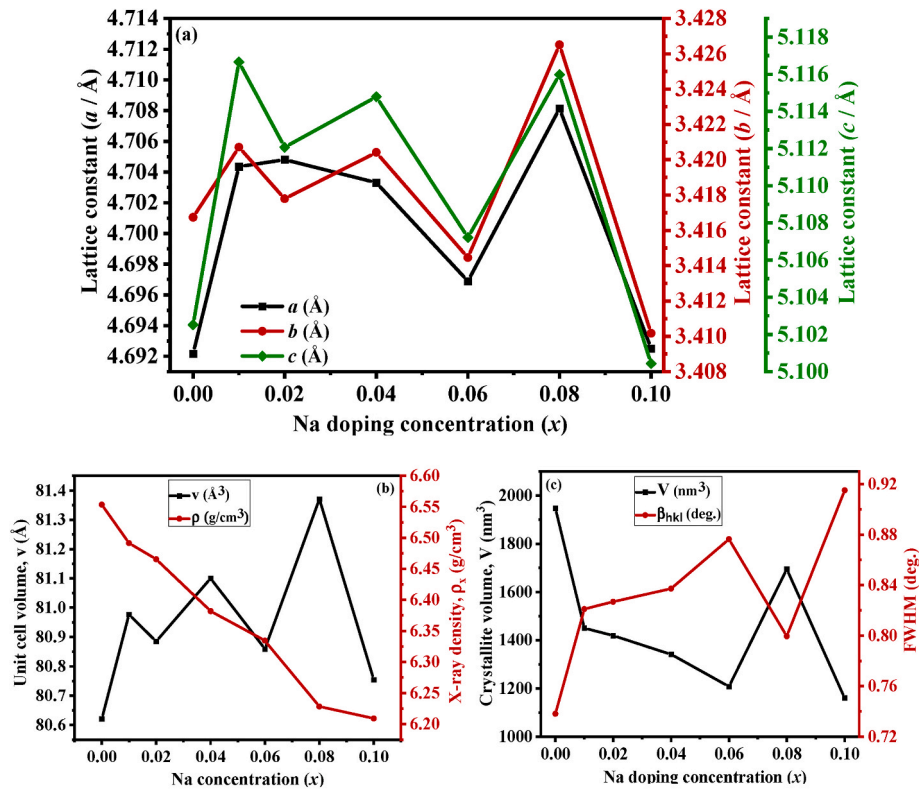


Fig. 4. The variation of (a) lattice parameters (*a*, *b*, and *c*); (b) unit cell volume and x-ray density; and (c) average FWHM and average crystallite volume of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders with Na doping concentration (*x*).

Table 4

The Bragg's angle (2θ), FWHM (β_{hkl}), Crystallite size (*D*) and inter-planar distance (*d*) of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ (*x* = 0–0.10) for (200) diffraction peak.

Na ⁺ Content (<i>x</i>)	Bragg's angle (2θ) (deg.)	FWHM β_{hkl} (deg.)	<i>D</i> (nm)	Inter planar distance (<i>d</i>) (Å)
0	38.920	0.655	12.8643	2.3122
0.01	38.901	0.7052	11.9471	2.3133
0.02	38.876	0.7228	11.6548	2.3147
0.04	38.821	0.6982	12.0643	2.3178
0.06	38.811	0.7403	11.3769	2.3184
0.08	38.768	0.6877	12.2470	2.3209
0.10	38.759	0.7357	11.4464	2.3214

3. Results and discussion

3.1. Powder X-ray diffraction (XRD) analysis

The XRD pattern of the $\text{Cu}_{1-x}\text{Na}_x\text{O}$ (0, 1, 2, 4, 6, 8, 10 mol% Na) powders calcined in an air atmosphere at 450 °C for 3 h are shown in Fig. 2(a). All the reflection peaks in the XRD pattern matched well with JCPDS card number 45-0937 of bulk CuO, with lattice parameters of $a = 4.6837$ Å, $b = 3.4226$ Å, $c = 5.1288$ Å and β (angle) = 99.5400° and space group C 2/c. The diffraction peaks of $\text{Cu}_{0.99}\text{Na}_{0.01}\text{O}$ sample found at 32.41°, 35.54°, 38.77°, 48.82°, 53.53°, 58.33°, 61.59°, 66.23°, 68.10°, 72.51°, and 75.23° obtained for the (−110), (002), (200), (−202), (020), (202), (−113), (−311), (113), (311) and (−222) planes correspond to a monoclinic symmetry structure. There are no extra peaks relating to secondary phase were obtained for $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples, indicating that the sodium ions are successfully substituted into the lattice site of Cu^{2+} without altering the CuO crystal structure. According to the XRD pattern, all the synthesized $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples were polycrystalline in nature. Also, the observed XRD intensity of the diffraction peaks decreases continuously up to $x = 0.06$, then strongly increased

and is maximum at $x = 0.08$ for Na doped CuO with increasing Na doping concentration. This intensity variation may be attributed to the reduction in crystallinity of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ [22]. The effect of sodium concentration on the mean crystallite size (*D*) of the ordered crystalline domains was estimated using the Debye-Scherrer formula [16]:

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta} \quad (3)$$

in which, *K* is shape factor constant (equal to 0.9), β_{hkl} is the peak width at FWHM (in radian), λ is the X-ray wavelength for Cu-target K_{α} radiation (1.5406 Å), and θ is the Bragg diffraction angle obtained from the 2θ value.

As shown in Fig. 3(a), the mean crystallite size was decreased with an increase in the doping concentration of Na into CuO matrix except at $x = 0.08$, where the sodium atoms have trapped in the nonequilibrium position from the equilibrium position. This reduction in crystallite size demonstrates the decreasing crystallinity of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples and can be attributed to the lattice distortion of CuO due to the incorporation of Na.

In addition, micro-structural parameters, such as the dislocation density (δ) and lattice-strain (ϵ) can be evaluated using the Williamson–Smallman's relation and Stokes–Wilson's equation, respectively as:

$$\delta = \frac{1}{D^2} \quad (4)$$

$$\text{and } \epsilon = \frac{\beta_{hkl} \cos \theta}{4} \quad (5)$$

It can be evidenced from Fig. 3(b and c), that the dislocation density and the micro-strain increased constantly on Na doping in the CuO as a result of decreased crystallite size and increased lattice defects except at $x = 0.08$. The calculated structural parameters were demonstrated in Table 2.

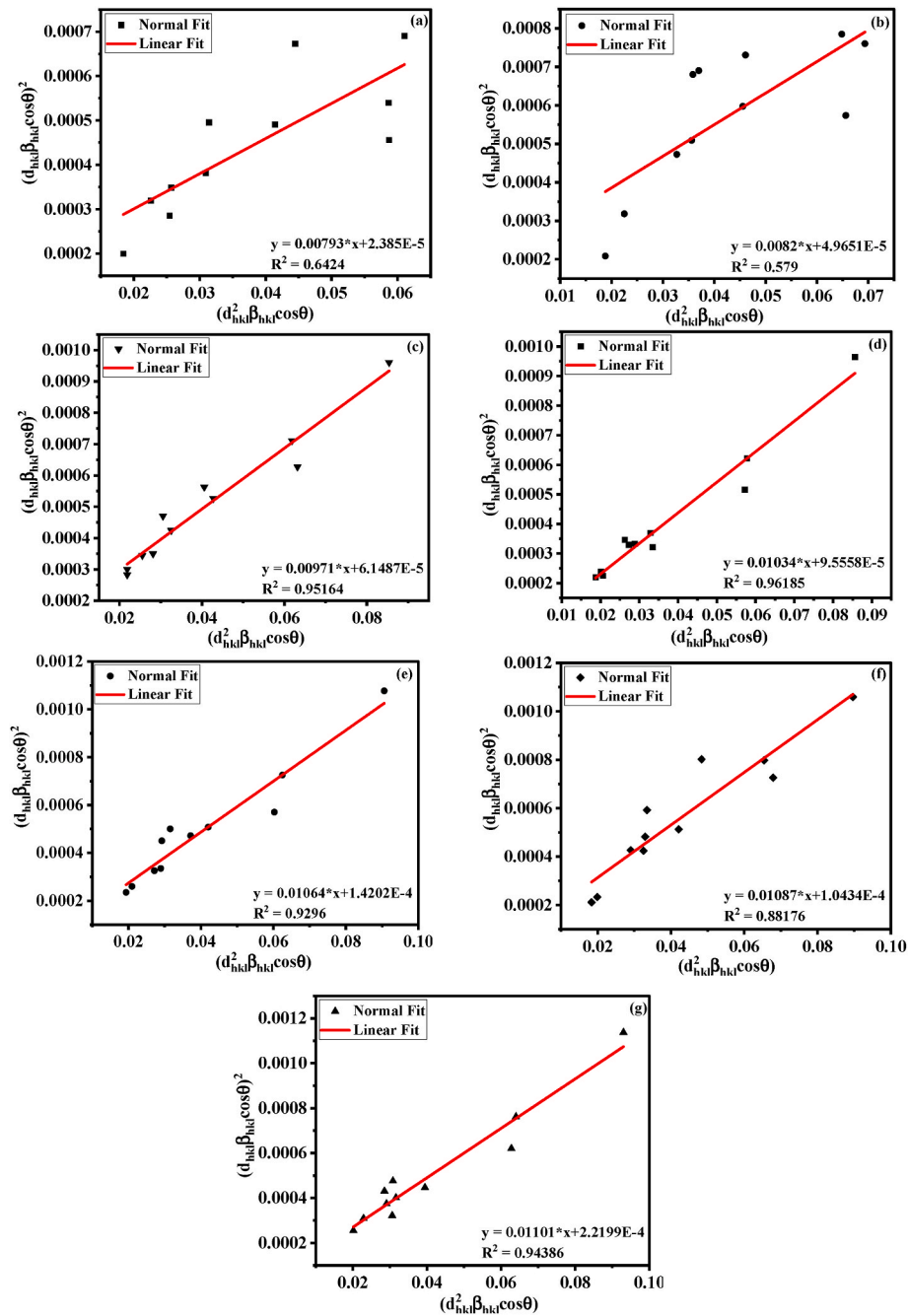


Fig. 5. Linear fit plots of Size-Strain plot (SSP) method for calculating crystallite size (D), dislocation density (δ), and lattice strain (ϵ) of a pure CuO NPs, b–g Na-doped CuO NPs.

Table 5

The average values of crystallite size (D), dislocation density (δ), and lattice strain (ϵ) of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders, calculated according to Size-strain plot (SSP) method.

Na^+ content (x)	D_{SSP} (nm)	$\delta_{\text{SSP}} \times 10^{-3}$ (nm^{-2})	$\epsilon_{\text{SSP}} \times 10^{-2}$
0	18.262	2.999	0.976
0.01	17.660	3.206	1.409
0.02	14.914	4.496	1.568
0.04	14.005	5.098	1.955
0.06	13.610	5.398	2.383
0.08	13.323	5.634	2.043
0.10	13.153	5.78	2.979

The lattice parameters a , b , and c of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders were evaluated from the interplanar distances d_{200} , d_{020} , and d_{002} using the following relation for monoclinic crystal structure [52]:

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \text{ in } \text{\AA} \quad (6)$$

where $a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$ and d is the interplanar spacing between the atoms, α , β , and γ are the inter-axial angles, and h , k , l are the Miller indices of lattice planes.

The lattice parameters (a , b , and c) and the inter-axial angle (β) obtained are listed in Table 3. The variation of estimated values of the lattice constants a , b , and c as a function of Na doping concentration is shown in Fig. 4(a). It can be observed that all the lattice parameters are

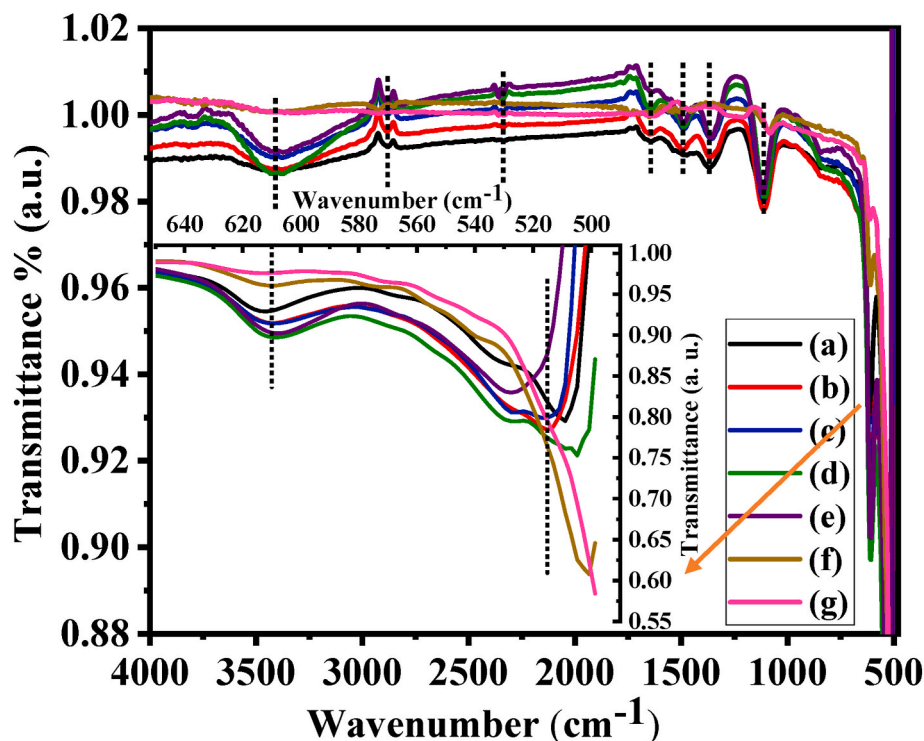


Fig. 6. FTIR spectra of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders for (a) pure, (b) 0.01, (c) 0.02, (d) 0.04, (e) 0.06, (f) 0.08, and (g) 0.10. Inset shows the magnified view of the stretching modes of Cu–O bond.

Table 6

FTIR peaks and their assignments of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders ($x = 0\text{--}0.10$).

Assignments	Wavenumber (cm^{-1})						
	$x = 0$	$x = 0.01$	$x = 0.02$	$x = 0.04$	$x = 0.06$	$x = 0.08$	$x = 0.10$
O–H stretching mode	3384	3397	3399	3340	3401	3410	3410
C–H stretching vibration	2880	2882	2882	2883.5	2883	2883	2885
Na–O signature	2336	2338	2337	2339	2339	2341	2341
$\nu(\text{C}=\text{O})$	1642	1645	1645	1645	1648	1650	1650
O–H stretching vibrations	1485	1492	1493	1493	1495	1500	1500
C–H stretching mode	1365	1365	1360	1359.5	1359.5	1367	1367
C–O stretching mode	1119	1112	1113.5	1109.5	1117.5	1088	1083
Cu–O stretching mode	612	610	610	608	607	611	614
Cu–O stretching vibration	509	514	515	505	527	530	530

first increases and then strongly reduced except at $x = 0.08$ as the sodium concentration increased. The lattice parameters a , b , and c were evaluated as 4.692, 3.416, and 5.102 Å for undoped CuO; and 4.692, 3.410, and 5.100 Å for $\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$ nano-powders, respectively. This characteristic behaviour is resulting from the tensile strain and stress developed by sodium dopants on the surface of CuO [20].

The crystallite volume (V), the unit cell volume (v), and the X-ray density ($\rho_{x\text{-ray}}$) were calculated using the following relations for

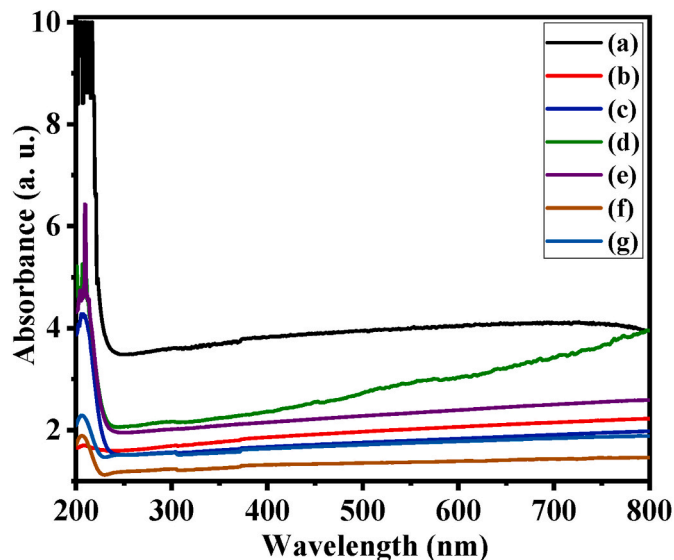


Fig. 7. UV–Vis optical absorption of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders for (a) pure, (b) 0.01, (c) 0.02, (d) 0.04, (e) 0.06, (f) 0.08, and (g) 0.10.

monoclinic system as

$$V = D^3 \text{ in } (\text{nm})^3, \quad (7)$$

$$v = abc \sin \beta \text{ in } (\text{\AA})^3, \quad (8)$$

$$\text{and } \rho_{x\text{-ray}} = \frac{ZM_w}{N_A v} \text{ in } (\text{g} / \text{cm}^3), \quad (9)$$

where, Z is the number of atoms or molecules per unit cell, M_w is the molecular weight, v is the volume of the unit cell, and N_A is the

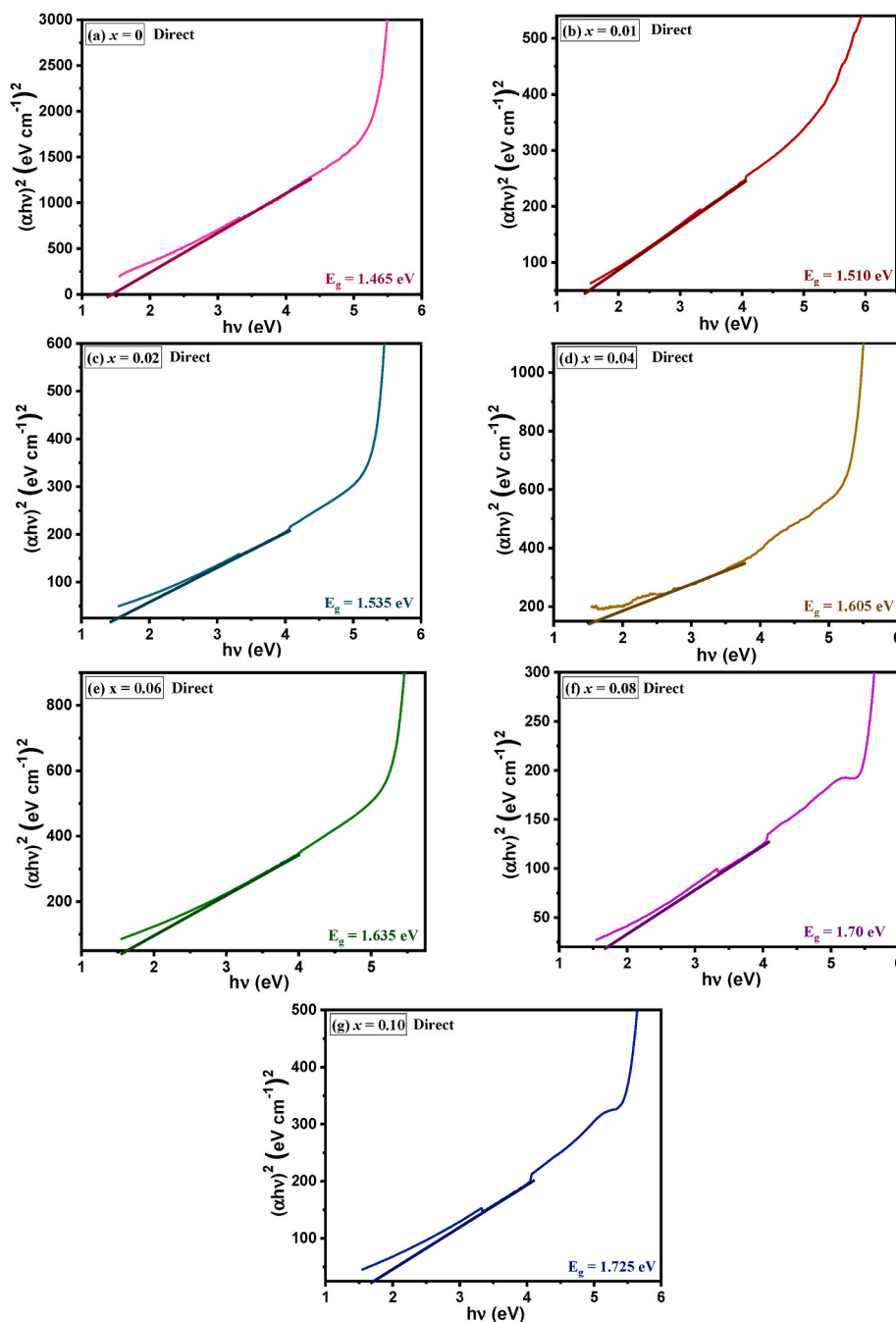


Fig. 8. Tauc's plot (direct band gap) of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders for (a) pure, (b) 0.01, (c) 0.02, (d) 0.04, (e) 0.06, (f) 0.08, and (g) 0.10.

Avogadro's number.

The observed reduction in x-ray volume density and the variation of unit cell volume with increasing Na doping concentration is shown in Fig. 4(b). This effect in x-ray density may be assigned to the reduced growth rate of CuO nanoparticles due to the decreasing adatom mobility in the host lattice over Na doping [53]. Fig. 4(c) shows the variation of average crystallite volume and average FWHM of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ as a function of Na dopant concentration. Moreover, the unit cell volume of Na doped samples is enhanced compared to that of pure CuO with the addition of sodium as a consequence of the presence of the large number of surface atom dangling bonds [15].

The 2θ value, FWHM (β_{hkl}), crystallite size, and inter-planar distance of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ for (200) diffraction plane was provided in Table 4. These results indicate that the (200) diffraction peak of Na-doped samples have shifted towards lower angles when compared with that of the

undoped samples as seen in Fig. 2(b), which also confirms the successful incorporation of sodium into CuO matrix. This shift is due to the differences in the ionic radii of Cu^{2+} (0.73 nm) and Na^+ (1.02 Å) and is attributed to the distortion of lattice parameters [54].

The average crystallite size (D_{SSP}), and lattice strain (ϵ_{SSP}) were also analysed by the Size-Strain plot (SSP) method using the following relation [55]:

$$(\mathbf{d}_{\text{hkl}} \cdot \beta_{\text{hkl}} \cdot \cos \theta)^2 = \frac{k\lambda}{D} (\mathbf{d}_{\text{hkl}}^2 \cdot \beta_{\text{hkl}} \cdot \cos \theta) + \frac{\epsilon^2}{4} \quad (10)$$

From the linear fit of experimental data as shown in the Fig. 5 (a - g), the micro-strain (ϵ_{SSP}) was evaluated from the y-intercept, and the crystallite size (D_{SSP}) was obtained from the slope. The values determined for D , δ , and ϵ using SSP method were provided in Table 5. These D , δ , and ϵ values were almost similar to those values measured by

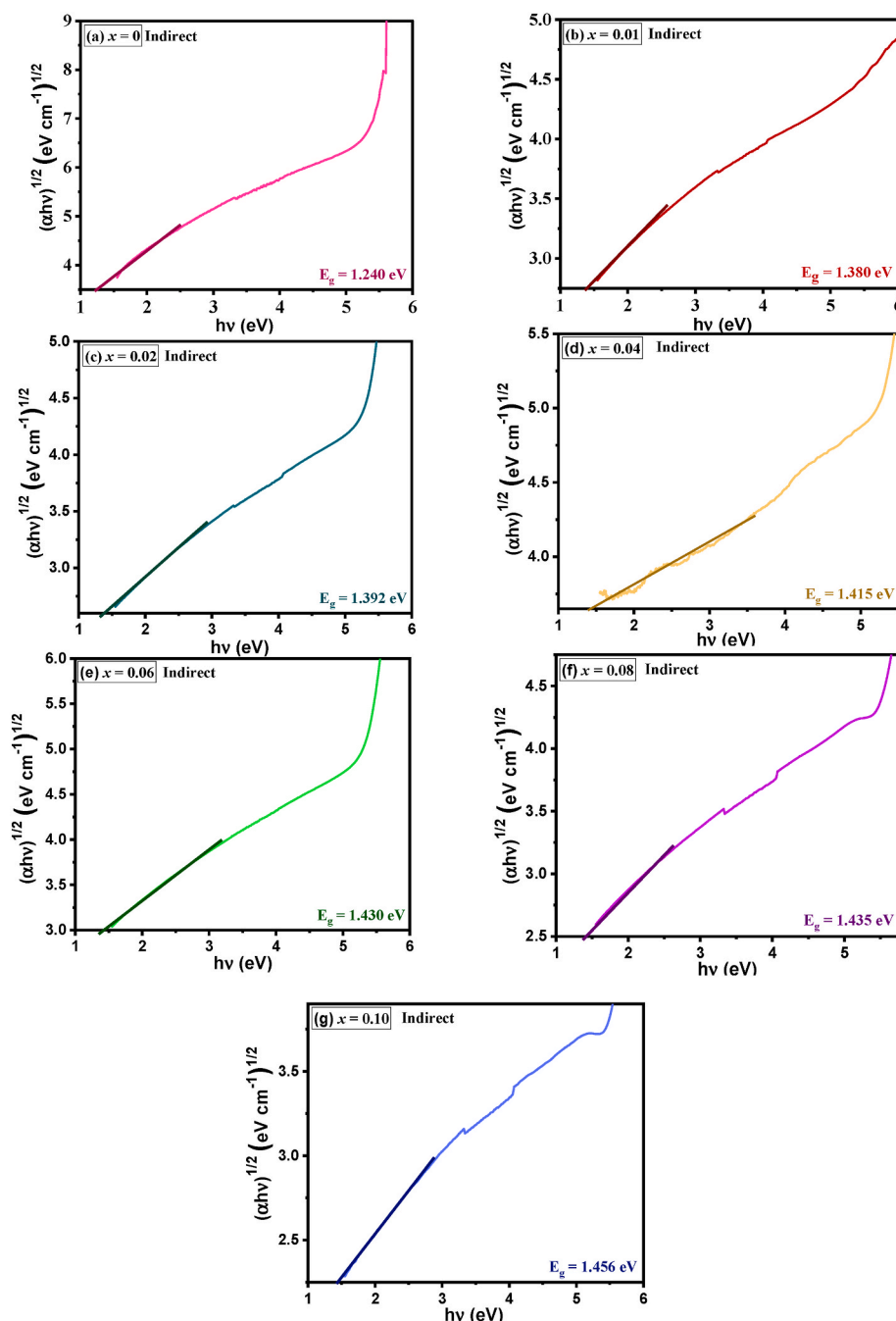


Fig. 9. Indirect band gap energies of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders for (a) pure, (b) 0.01, (c) 0.02, (d) 0.04, (e) 0.06, (f) 0.08, and (g) 0.10.

Debye – Scherrer method and their variation with Na doping concentration have shown in Fig. 3 (a – c). The values of crystallite size measured using SSP method was found to be reduced from 18.262 nm to 13.153 nm which an increasing amount of Na dopant concentration. However, the micro-strain evaluated from the Debye-Scherrer relation and the SSP method presents a large variation due to the averaging variance in the particle size distribution.

3.2. Fourier transform infrared spectrum (FTIR) analysis

The Fourier transform infrared (FTIR) spectroscopy is a technique used to identify various functional groups present in the samples by analysing different vibrational bands. Fig. 6(a–g) shows the FTIR pattern under the wavenumber range $4000\text{--}500\text{ cm}^{-1}$ of the pure and Na doped CuO nano-powders annealed at $450\text{ }^\circ\text{C}$ for 3 h in the atmosphere of air.

As shown in Fig. 6(b), the $\text{Cu}_{0.99}\text{Na}_{0.01}\text{O}$ sample exhibits a broad vibrational band between 3600 and 3100 cm^{-1} centred at 3400 cm^{-1} and a small absorption peak at 1492 cm^{-1} , which are attributed to the stretching vibrational modes of the hydroxyl group ($-\text{OH}$) [56]. The stretching modes of the vibration assigned to the C–H molecule was obtained at 2880 cm^{-1} and 1364 cm^{-1} [57]. The characteristic absorption peaks at 1645 cm^{-1} and 1112 cm^{-1} were corresponding to the stretching vibrations of C = O and C–O, respectively [58]. The presence these molecules is attributed to the improper thermal decomposition of the acetate group. The vibrational modes of metal – oxygen bonds were basically observed below the wavenumber of 1000 cm^{-1} . Accordingly, the frequency stretching modes associated to Cu–O bond of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples have been obtained around 610 and 514 cm^{-1} [59]. The signature of sodium may be confirmed by the sharp absorption peak of Na–O bond at 2340 cm^{-1} in Na doped samples as compared to pure CuO

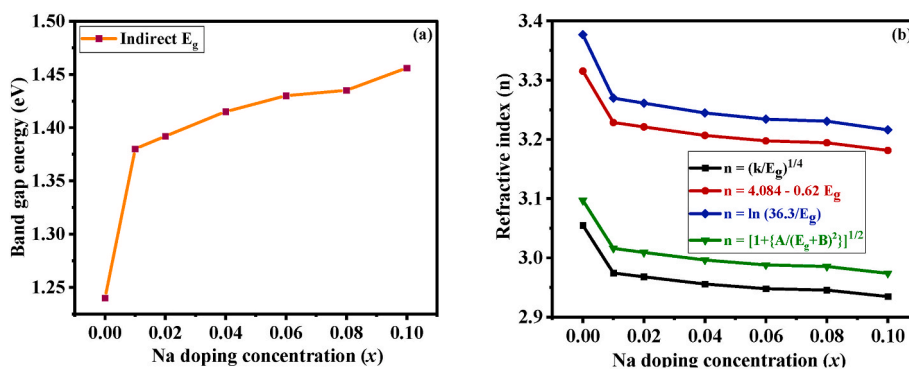


Fig. 10. Calculated variation of (a) Indirect band gap (E_g); and (b) Refractive index (n) as a function of Na doping concentration in $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders.

Table 7

The estimated values of Optical bandgap energy (E_g) and the refractive index (n) of the polycrystalline $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples.

Na ⁺ content (x)	E_g (eV)		Refractive index (n)			
	Direct	Indirect	(108/ E_g) ^{1/4}	4.084 - 0.62 E_g	ln (36.3/ E_g)	$[1 + \frac{A}{(B + E_g)^2}]^{1/2}$
0	1.465	1.240	3.055	3.315	3.377	3.097
0.01	1.510	1.380	2.974	3.228	3.27	3.016
0.02	1.535	1.392	2.968	3.221	3.261	3.009
0.04	1.605	1.415	2.956	3.207	3.245	2.996
0.06	1.635	1.430	2.948	3.197	3.234	2.988
0.08	1.700	1.435	2.945	3.194	3.231	2.985
0.10	1.725	1.456	2.935	3.181	3.216	2.974

sample, in which it is not present [60]. Furthermore, no additional IR active vibrational peaks were obtained in the wavenumber range of 605–660 cm^{-1} confirming the non-existence of secondary phase, i.e., Cu_2O phase [61]. It is also observed from the XRD results that the as-prepared nano-powders does not manifest the presence of cuprous oxide (Cu_2O). Hence, the FTIR analysis shows that the Na is successfully substituted into CuO monoclinic crystal lattice. To analyse the doping

effect of sodium, all the FTIR patterns of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ ($x = 0, 0.01, 0.02, 0.04, 0.06, 0.08$, and 0.10) nano-materials are plotted at the same scale for better comparison and the absorption peaks along with their assignments are tabulated in Table 6. The vibrational peaks of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ become sharper with increasing sodium doping content upto $x = 0.04$, then gradually decreases and appeared to be dull. Moreover, the vibrational peaks shifting towards the higher wavenumber (blue shifted) with an increase in doping concentration of sodium is observed may be due to smaller crystalline size of Na-doped CuO nano-powders in comparison to that of pure CuO samples [62,63].

3.3. UV-visible analysis

The UV-Visible absorption spectroscopy was used to analyse the bandgap energy (E_g) as well as the mode of electronic transitions. The absorption spectra of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders in the region 200–800 nm were shown in Fig. 7. A strong fundamental peak about 208 nm and an absorption edge at 304 nm were observed may be due to direct transition of electrons and surface plasmon resonance of metal oxide, respectively [64,65]. The fundamental absorption peak of the coprecipitation synthesized $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders was shifted from 208.5 nm to 205.5 nm with increasing sodium dopant concentration as shown

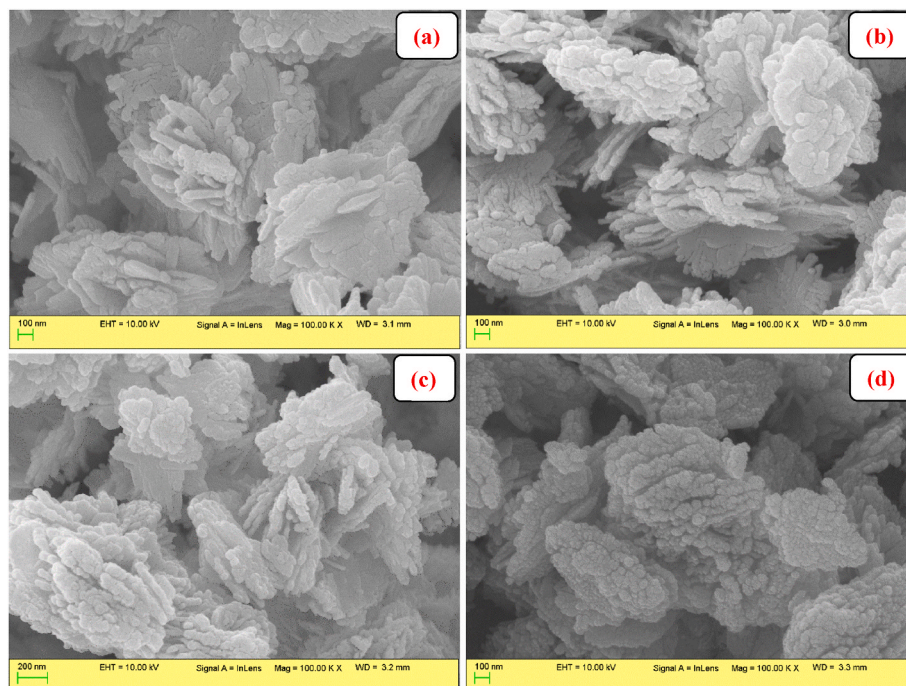


Fig. 11. FESEM images of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders; (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.06$, and (d) $x = 0.10$, respectively.

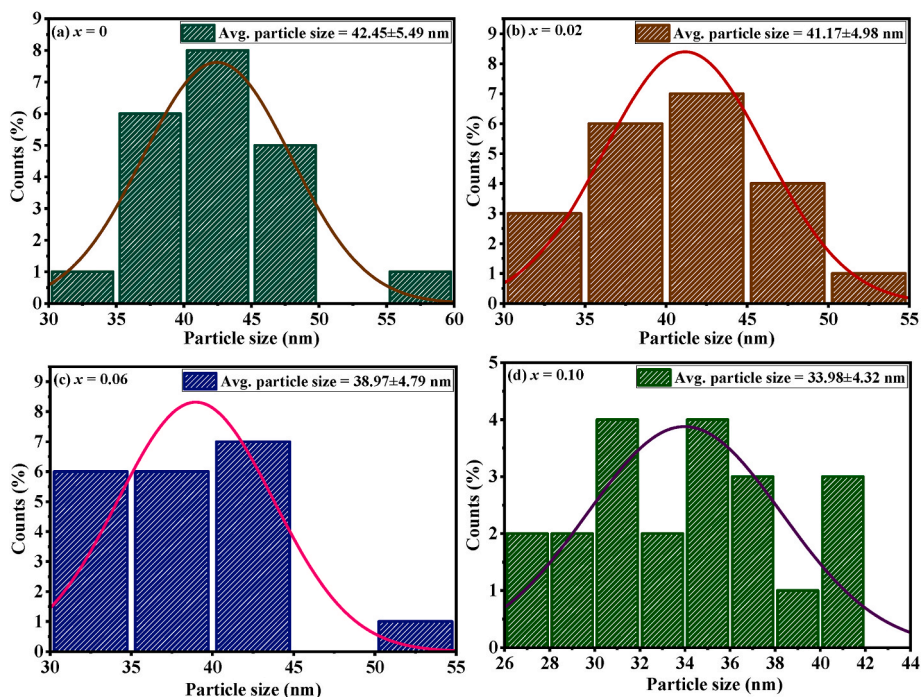


Fig. 12. Histogram representation (FESEM micrographs) of particle size distribution of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders; (a) $x = 0$; (b) $x = 0.02$; (c) $x = 0.06$; and (d) $x = 0.10$, respectively.

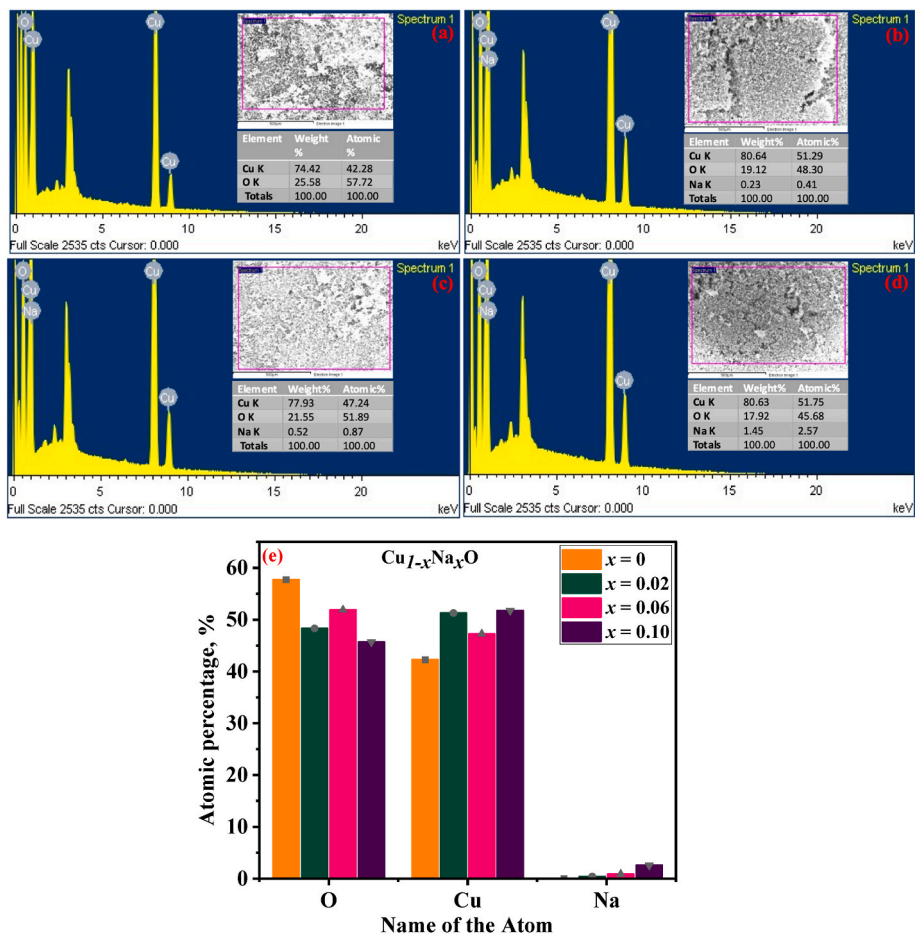


Fig. 13. The energy dispersive X-ray analysis (EDAX) spectra of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders; (a) $x = 0$; (b) $x = 0.02$; (c) $x = 0.06$; and (d) $x = 0.10$, respectively, inset tables shows the elemental composition. (e) is the corresponding histogram representation in atomic percentage.

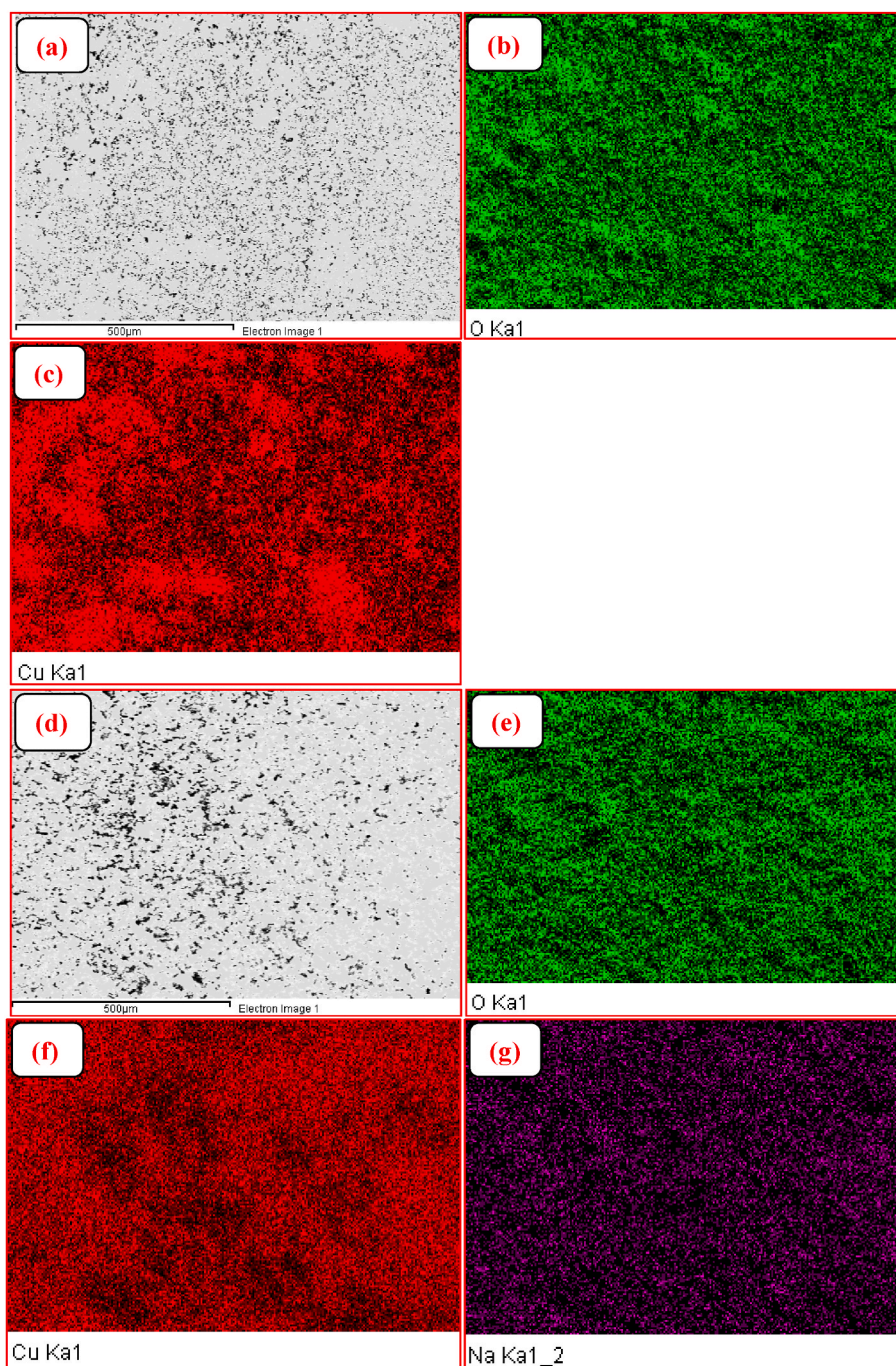


Fig. 14. (a) EDAX element layered image of pure CuO, and (b - c) elemental mapping for O, and Cu respectively; (d) EDAX element layered image of $\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$, (e - g) elemental mapping images for O, Cu and Na respectively.

in Fig. 7. Hence, it can be clear that the optical properties of pure and sodium doped CuO samples largely depends on the particle crystallite size and doping concentration of Na [66]. The direct/indirect bandgap energy (E_g) value is estimated by the Tauc's equation [67] as

$$(\alpha h\nu)^r = A (h\nu - E_g) \quad (11)$$

where, α is optical absorption coefficient (cm^{-1}), $h\nu$ is photon energy (eV), A is the energy independent constant related to the material, r is an exponent is equal to 2 for a direct electronic transition and $\frac{1}{2}$ for an indirect electronic transition, and E_g is the bandgap energy (eV). The indirect and direct bandgap (E_g) can be calculated by extrapolating the linear portion of the curve to the photon energy axis. The plots of $(\alpha h\nu)^2$

versus $h\nu$ and $(\alpha h\nu)^{1/2}$ versus $h\nu$ of as-synthesized samples were given in Figs. 8 and 9, used to evaluate the direct and indirect E_g values, respectively. The indirect optical band gap (E_g) energy values of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders obtained are in the range of 1.240–1.456 eV, which were higher as compared to the band gap value of bulk CuO (1.2 eV in bulk) confirms the quantum confinement effect. Further, the measured band gap value increases with increasing sodium doping concentration as depicted in Fig. 10(a). This characteristic variation of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ semiconducting materials is mainly due to the trapping of free charge carriers, and lattice deformation due to the strain caused by surface defects [53,68]. Therefore, the blue shift in the band gap energy makes the Na doped CuO samples ideal for the applications of semiconductor devices including photo-detectors, photovoltaic cells, and

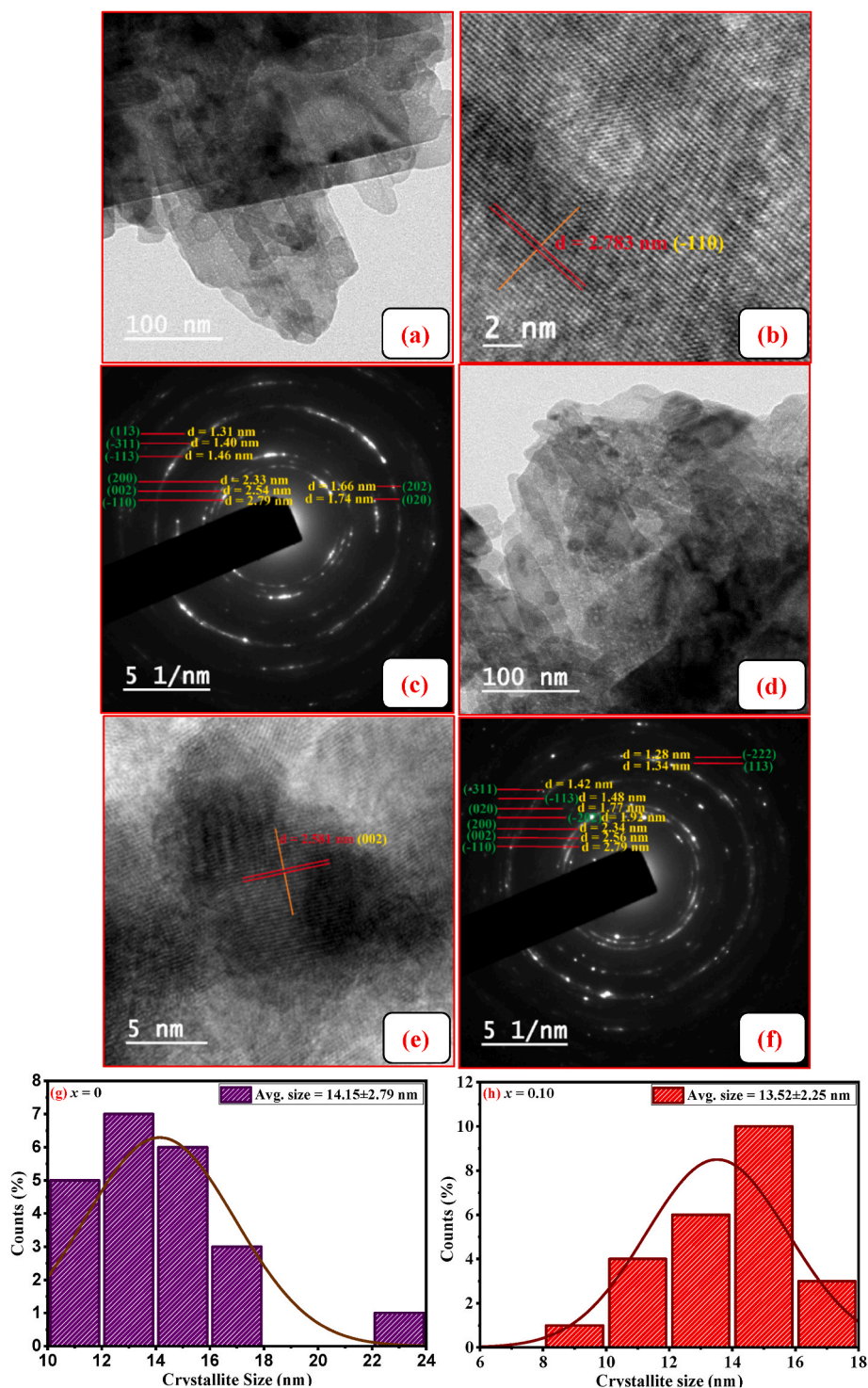


Fig. 15. TEM bright-field images of the as-synthesized (a) pure CuO and (d) Cu_{0.90}Na_{0.10}O NPs; and (b, e) are the corresponding HRTEM micrographs, respectively; (c, f) are the typical corresponding selective area electron diffraction (SAED) patterns, respectively; (g, h) are the corresponding range of histograms with the Gauss fitting curve for evaluating the average crystallite size and its distribution, respectively.

photo-amplifiers [16]. The indirect/direct E_g values obtained were listed in Table 7. The values of direct energy band gap of Cu_{1-x}Na_xO are found to be 1.465–1.725 eV, which are in close agreement with the reported values of 1.34–1.50 eV by Anu et al. [15] in the literature.

The optical refractive index (n) of semiconductor nanomaterials was estimated from the above calculated bandgap energy (E_g) values using four distinct atomic models, named as Ravindra et al. [69], Ravindra and Gupta [70,71], Reddy et al. [72], and Herve and Vandamme [52] by

using the following relations:

$$n^4 \cdot E_g = 108 \quad (12)$$

$$n = 4.084 - 0.62 E_g \quad (13)$$

$$E_g \cdot e^n = 36.3 \quad (14)$$

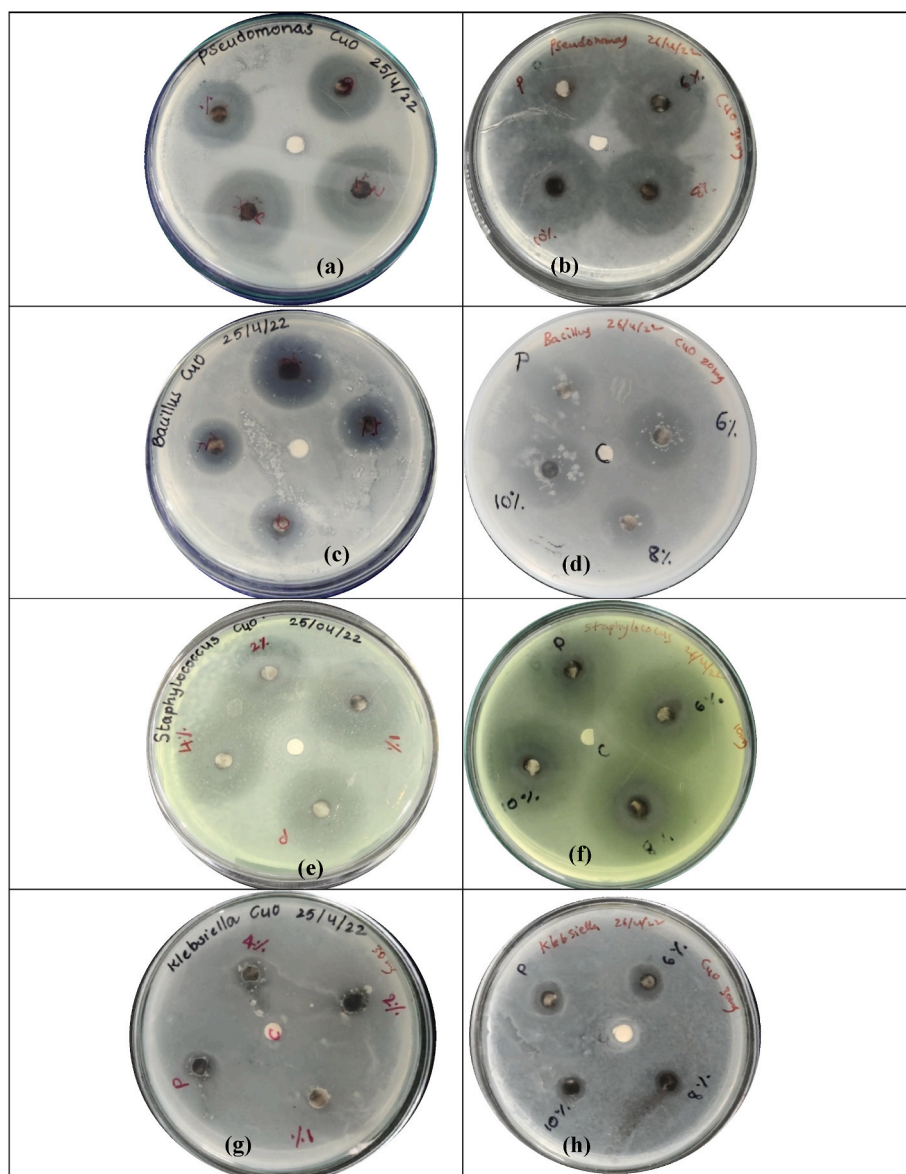


Fig. 16. Antibacterial activity of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ with different sodium concentrations against the bacterial strains (a - b) *P. Aeruginosa*, (c - d) *B. subtilis*, (e - f) *S. aureus*, and (g - h) *K. pneumoniae*.

$$n = \sqrt{1 + \left[\frac{A}{E_g + B} \right]^2} \quad (15)$$

where the values of numerical constants A and B are 13.6 and 3.4 eV, respectively.

Fig. 10 (b) shows that the estimated refractive index (n) is larger than 2 and it was found to decrease with increasing Na doping concentration. The refractive index (n) values obtained at band gap region are in the range of 3.055–2.935, 3.315–3.181, 3.377–3.216, and 3.097–2.974 according to the four models, Ravindra et al., Ravindra and Gupta, Reddy et al., and Herve and Vandamme respectively. Hence it was evident that, pure CuO and $\text{Cu}_{0.99}\text{Na}_{0.01}\text{O}$ have high refractive index, while lower value of refractive index corresponds to $\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$ (Table 7). All the four atomic models show a similar fashion. Generally, the refractive index is used to measure the transparency of a semiconductor optical material to the incident radiation. Therefore, these results depict the Na doped CuO samples have been used as integrated optoelectronic devices and photovoltaic cells.

3.4. Field emission scanning electron microscopy (FESEM) analysis

The size, shape and surface morphology of the as-prepared $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders annealed at 450 °C for 3 h were examined using FESEM. The FESEM images of pure and selected Na doped CuO materials were presented in Fig. 11(a-d) shows irregular spherical morphology of the particles. The values of mean particle size were 42.45 ± 5.49 , 41.17 ± 4.98 , 38.97 ± 4.79 , and 33.98 ± 4.32 nm for pure, 2, 6, and 10% Na-doped CuO, respectively estimated by using the particle distribution curves as shown in Fig. 12(a-d). Clearly, the average particle size observed by FESEM micrographs is slightly larger in comparison with XRD and HRTEM and is due to the self-aggregation of many nano-particles [18]. Also, a slight variation in the particle size was observed in Na doped CuO NPs when compared with pure CuO NPs. Moreover, the small nuclear spherical particles are self-agglomerated into cauliflower-shaped structures and also align themselves in hierarchical growth to form closely oriented flake-like structures. The mean size of the composite nanocauliflowers and nanoflake-like structures depends on the Na doping concentration [24].

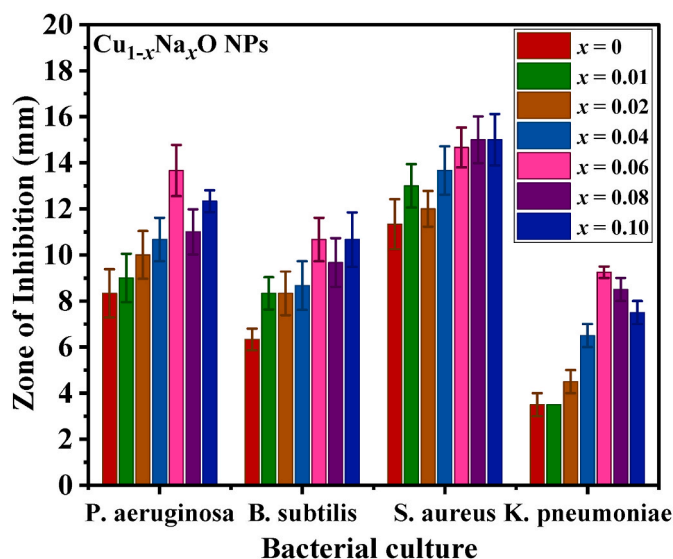


Fig. 17. Histogram representation of antibacterial activity of the compounds towards the *P. aeruginosa*, *B. subtilis*, *S. aureus* and *K. pneumoniae* bacteria. The values are Mean $\pm$ SD (n = 4). *P < 0.0001 Compared to control (Pure CuO).

3.5. Energy dispersive X-ray spectroscopy (EDAX) and mapping analysis

The EDAX compositional analysis was performed to observe the purity and formation of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powder samples. The EDAX spectra confirmed the presence of elements Cu K and O K alone in pure CuO; and Cu K, O K, and Na K in Na doped CuO samples (Fig. 13 (a) – (d)), which also reveals the successful incorporation of Na^+ at Cu^{2+} lattice sites in CuO crystal lattice [20]. The atomic ratios of Cu:O in pure CuO and Cu:O:Na in Na doped CuO were determined by the EDAX analysis revealed as histogram in Fig. 13(e). From Fig. 13(e), it was evident that the emission of sodium gradually increases with increasing sodium doping concentration in the as-prepared samples [19].

Moreover, the elemental mapping of each constituent element in the grown samples was studied by EDAX mapping measurements as depicted in Fig. 14 and it was observed that the Cu, O, and Na elements in $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples are uniformly distributed in composition [26,73]. Hence the Na-related prominent peak in all the EDAX spectra (Fig. 13 b–d) shows the occurrence of sodium atoms in the $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nanostructures.

3.6. High resolution transmission electron microscopy (HRTEM) analysis

Fig. 15 (a, b) shows the TEM and HR-TEM micrographs of pure CuO nano-powders synthesized using coprecipitation method. The interplanar spacing between the adjacent lattice planes of pure CuO was obtained 2.783 nm which corresponds to (–110) lattice plane. The SAED pattern of undoped CuO nanopowders was given in Fig. 15 (c), which shows bright and sharp spots as well as lattice planes showing poly-crystallite nature [54,65]. The observed SAED pattern clearly demonstrating the monoclinic crystal structure of pure CuO and the obtained HR-TEM results are in excellent agreement with PXRD pattern. The pure CuO nanopowders reveals agglomerated spherical and flakes like particles with mean particle size of 14.15 ± 2.79 nm (Fig. 15 (g)).

The TEM image of 10% Na-doped CuO ($\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$) sample (Fig. 15 (d)) depicts comparatively small particles of spherical and flakes-like structures. The TEM image also shows the formation of aggregated secondary particles from few primary nanoparticles, owing to their high surface areas and lower dimensions. The interplanar distance estimated from HRTEM image (Fig. 15 (e)) was 2.581 nm, which shows the presence of (002) plane in $\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$. The lattice plane reflections observed from the corresponding SAED pattern (Fig. 15 (f)) of $\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$ sample also reveals the monoclinic crystal structure. Fig. 15 (h) shows the histogram representation with Gauss fitting curve of $\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$ NPs and the average particle size is found to be 13.52 ± 2.25 nm, which is compared with the XRD result [74,75].

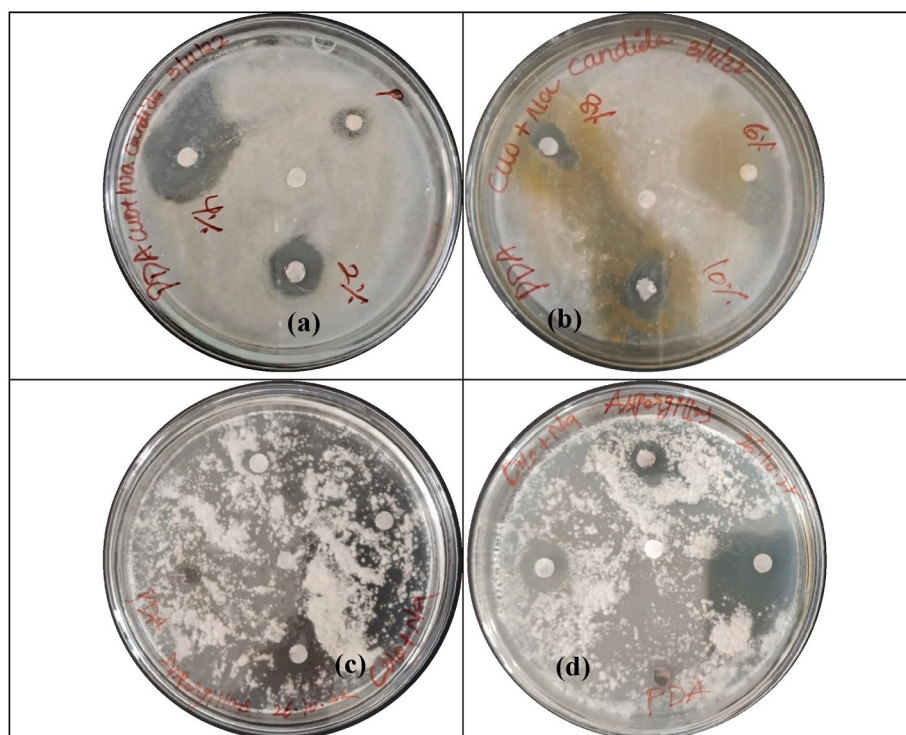


Fig. 18. Antifungal activity of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ NPs with different sodium concentrations against the fungal strains (a - b) *C. albicans*, and (c - d) *A. niger*.

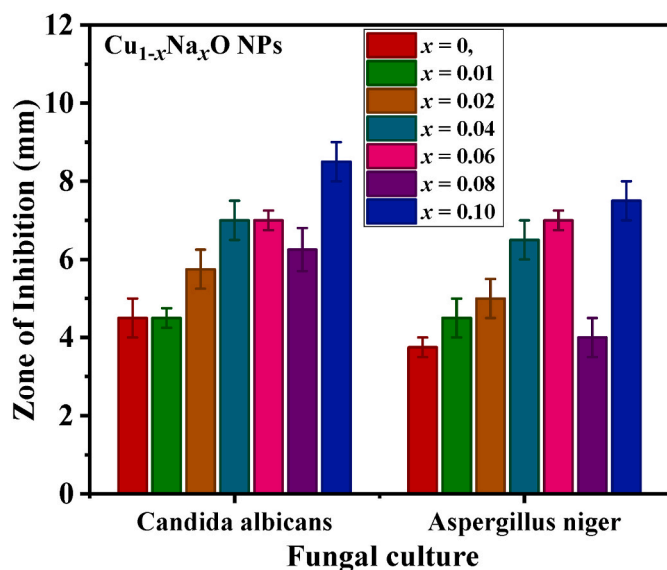


Fig. 19. Histogram representation of antifungal activity of the compounds towards the fungi *C. albicans* and *A. niger*. The values are Mean $\pm$ SD (n = 4). *P < 0.0001 Compared to control (Pure CuO).

3.7. Antimicrobial activity

The Antimicrobial activity of coprecipitation synthesized pure and Na substituted CuO NPs was tested by measuring the zone of inhibition (ZOI) with different Na doping concentrations (1, 2, 4, 6, 8, and 10%) against various bacterial and fungal strains. The antibacterial activity of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ samples is studied for two Gram positive bacterial strains (*Bacillus subtilis*, *Staphylococcus aureus*) and two Gram negative bacterial organisms (*Pseudomonas aeruginosa*, *Klebsiella pneumoniae*) by the zone of inhibition method, where the inhibition zone around each Petri dish is estimated in mm by using the meter ruler [50].

The inhibition of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nanoparticles is demonstrated against various pathogenic bacteria as follows. The gram-negative bacteria cell has a thin wall of single layer peptidoglycan (PG) molecule, whereas the outer membrane of gram-positive bacteria cell is a thick wall having multi-layer peptidoglycans. As the peptidoglycan is negative charged, the presence of PG macromolecules produces an overall negative charge in both type of bacteria. However, due to a greater number of peptidoglycans, the gram-positive bacteria are more negatively charged than the gram-negative bacteria. Hence, there is an electrostatic attraction between CuO nanoparticles and bacteria cell walls because of positive charge of the CuO NPs [49]. This interaction of more positive Cu ions with negative peptidoglycan ions over the surface of bacteria will disrupt the outer membrane or cell wall.

Fig. 16 shows the observed zone of inhibition around each disc of pure and Na doped CuO NPs over gram-positive bacteria species (*Bacillus subtilis* and *Staphylococcus aureus*); and gram-negative bacteria (*Pseudomonas aeruginosa* and *Klebsiella pneumoniae*). The results showed that, for gram positive bacteria, the inhibition zone is increased with increasing Na doping concentration, which is attributed to reduced crystallite size [48]. The as-synthesized NPs with large particle size demonstrated bacteriostatic effect, while those with small size showed bactericidal activity [4]. The highest radial diameter of the inhibitory zone observed for $\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$ of *B. subtilis* and *S. aureus* was 10.67 ± 0.94 and 15 ± 1.11 mm, respectively (Fig. 17). $\text{Cu}_{1-x}\text{Na}_x\text{O}$ NPs exhibited higher antibacterial activity against *S. aureus* than *B. subtilis* [76]. Interestingly, in case of gram-negative bacteria, the effect of Na^+ doping content on the antibacterial activity of CuO NPs shows different results. Apparently, $\text{Cu}_{0.94}\text{Na}_{0.06}\text{O}$ NPs presented the best antibacterial effect with observed maximum zone of inhibition 13.67 ± 1.11 and 9.25 ± 0.25 mm for *P. aeruginosa* and *K. pneumoniae*, respectively (Fig. 17).

When the Na^+ doping concentration further enhanced beyond 6%, Na-doped CuO NPs exhibited decreased antibacterial activity [17]. It can be observed that, the zone of inhibition for all the as-grown NPs follows the sequence as *S. aureus* > *P. aeruginosa* > *B. subtilis* > *K. pneumoniae*. This significant variation of antibacterial activity towards Gram-negative and Gram-positive bacteria may be assigned to the differences in their metabolism, net negative charge, cell structure, level of interaction of bacteria species with $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nanoparticles [15]. The superior antibacterial activity of Na doped CuO materials may also due to the synergetic interaction between sodium and ZnO nanoparticles as a result of the greater formation of reactive oxygen species (ROS) when compared to the individual materials. Thus, CuO NPs with addition of Na exhibited synergistic antibacterial activity against *S. aureus* and *P. aeruginosa* bacteria [59].

3.8. Antifungal activity

The antifungal study of pure and Na-doped CuO nanoparticles were shown in Fig. 18. The as-prepared nanoparticles with different Na concentrations were subjected to their antifungal activity against polymorphic fungus *C. albicans* and filamentous fungus *A. niger*. The $\text{Cu}_{1-x}\text{Na}_x\text{O}$ NPs presented higher antifungal activity against *C. albicans* with the maximum zone of inhibition of 8.5 ± 0.5 mm, followed by *A. niger* whose highest zone of inhibition was measured to be 7.5 ± 0.5 mm, respectively. The pure and Na-doped CuO NPs shows increased tendency of the zone of inhibition against *A. niger* except for 8% Na doping content, where the crystallite size of the NPs is observed to be high (Fig. 19) [51]. Clearly, the antifungal activity of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nanoparticles increases with an increase in the Na doping concentration and it is size dependent. Similarly, the pure and Na-graded CuO NPs shows active antifungal effect against the fungus *C. albicans* and the zone of inhibition is found to be increasing at lower Na doping content, but no significant change was observed in the zone of inhibition for high dopant concentration [20]. However, the highest antifungal activity against *C. albicans* was obtained for $\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$ nanoparticles. At high doping concentration of Na, the metal ions liberated from $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nanoparticles may increase the antifungal effect by damaging the cell wall or membrane and will diffuse into cells [77,78]. Hence, Na doped CuO NPs showed profound antifungal activity against fungi *C. albicans* and *A. niger* [79].

4. Conclusion

We have reported the synthesis of pure and sodium doped CuO cauliflower-shaped and flake-like nanostructures by a simple coprecipitation route after thermal treatment at 450°C for 3 h. The $\text{Cu}_{1-x}\text{Na}_x\text{O}$ nano-powders with single phase was confirmed by XRD and SAED and present the monoclinic crystal structure. The band gap energy of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ materials is found to be increased and the refractive index, which is estimated based on the measured band gap energy, is reduced with increasing Na doping concentration. The existence of Na^+ in CuO was evidenced from the Na–O absorption peak at 2340 cm^{-1} in FTIR and sodium related peak in EDAX spectra. The FESEM and HR-TEM studies predicted that the irregular spherical NPs are agglomerated into nano cauliflower-shaped and flake-like structures alignment and the mean particle size changed according to Na doping concentration. The antibacterial studies of pure and Na doped CuO NPs confirmed an increased antibacterial activity against Gram positive (*S. aureus* and *B. subtilis*) bacterial strains except for $x = 0.08$, while $\text{Cu}_{0.94}\text{Na}_{0.06}\text{O}$ NPs shows high antibacterial effect against Gram negative (*P. aeruginosa* and *K. pneumoniae*) bacteria. The antifungal activity of $\text{Cu}_{1-x}\text{Na}_x\text{O}$ NPs shows an increased zone of inhibition against fungus *A. niger*, while the highest inhibitory zone against *C. albicans* is achieved for $\text{Cu}_{0.90}\text{Na}_{0.10}\text{O}$ nanoparticles. It is concluded that the resulted coprecipitation synthesized $\text{Cu}_{1-x}\text{Na}_x\text{O}$ NPs showed significant antibacterial and high antifungal activities. Thus, the antimicrobial studies of pure and sodium doped CuO

NPs elicited their usage in future medical applications as promising antifungal drugs and the treatment of dangerous bacterial infections.

CRedit authorship contribution statement

B. Nageswara Rao: Experimentation, Writing – original draft. **P. Tirupathi Rao:** Visualization, Investigation. **Sk.Esub Basha:** Experimentation, Writing – original draft. **D.S.L. Prasanna:** Writing – review & editing. **K. Samatha:** Visualization, Investigation. **R.K. Ramachandra:** Conceptualization, Methodology, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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