

Microstructural Evolution and Optical Properties of Hydrothermally Synthesized CuO/ZrO₂ Nanocomposites

Pullarao Teneti

Acharya Nagarjuna University

P. Naresh

Velagapudi Ramakrishna Siddhartha School of Engineering, Siddhartha Academy of Higher Education
(Deemed to be University)

G. Sreedevi

Prasad V Potluri Siddhartha Institute of Technology

G. Nagaraju

gnaga9@gmail.com

Acharya Nagarjuna University

Research Article

Keywords: CuO/ZrO₂ nanocomposite, Hydrothermal synthesis, Phase evolution, Microstructural properties, Optical band gap, Luminescence

Posted Date: August 7th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10559067/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Chemical Papers on October 14th, 2026.
See the published version at <https://doi.org/10.1007/s11696-026-05778-2>.

Microstructural Evolution and Optical Properties of Hydrothermally Synthesized CuO/ZrO₂ Nanocomposites

P. Teneti^{1,3}, P. Naresh², G. Sreedevi³, G. Nagaraju^{1,z}

¹ Department of Physics, Acharya Nagarjuna University, Guntur, Andhra Pradesh -522 510, India

² Department of Physics, Velagapudi Ramakrishna Siddhartha School of Engineering, Siddhartha Academy of Higher Education (Deemed to be University), Vijayawada – 520 007, India

³ Department of Physics, Prasad V Potluri Siddhartha Institute of Technology, Vijayawada, Andhra Pradesh—520 007, India

Abstract:

In this study, pure CuO, pure ZrO₂ nanoparticles (NPs) and CuO/ZrO₂ nanocomposite (NC) were synthesized via a solution assisted hydrothermal method at 150 °C and systematically investigated to understand the influence of CuO incorporation on the structural, optical and luminescence properties of ZrO₂. X-ray diffraction analysis confirmed the formation of monoclinic CuO and predominantly monoclinic ZrO₂, while the CuO/ZrO₂ NC exhibited partial stabilization of the tetragonal ZrO₂ phase. Williamson–Hall (WH) analysis revealed reduced lattice strain and dislocation density in the CuO/ZrO₂ NC. The average crystallite sizes were found to be 14.2 nm for CuO, 8.4 nm for ZrO₂ and ~38 nm for the CuO/ZrO₂ NC. SEM revealed agglomerated micron-sized particles assembled from nanoscale crystallites, while EDAX analysis confirmed the homogeneous distribution of Cu, Zr and O elements. FTIR spectra showed characteristic Cu–O and Zr–O vibrational modes, together with band broadening in the composite arising from interfacial interactions between the constituent oxides. DRS studies revealed optical band gaps of 2.44 eV for CuO, 4.04 eV for ZrO₂ and 3.64 eV for the CuO/ZrO₂ NC, indicating significant modification of the electronic structure after composite formation. PL studies demonstrated defect–assisted visible emissions associated with oxygen-vacancy-related states and interfacial defect centers. The combined structural and spectroscopic analyses revealed a strong correlation between phase evolution, microstructural modification and optical response, which may enhance the potential of CuO/ZrO₂ NCs for photocatalytic, sensing and optoelectronic applications.

Key words: CuO/ZrO₂ nanocomposite; Hydrothermal synthesis; Phase evolution; Microstructural properties; Optical band gap; Luminescence

^z Corresponding author: G. Nagaraju gnaga@gmail.com

1. Introduction:

Semiconductor nanomaterials have attracted considerable attention owing to their unique size-dependent structural, optical, electrical and catalytic properties. These materials play an important role in the development of low-cost, high-efficiency, and compact optoelectronic devices for applications in telecommunications, biomedical engineering, sensing and energy-related technologies [1, 2]. Despite progress in semiconductor nanostructures, understanding the relationship between composition, microstructure and optical response remains

a key challenge for the design of advanced functional materials. Among various semiconductor systems, copper-based nanomaterials have received considerable interest because of their excellent electrical and thermal conductivity, chemical stability, and cost-effectiveness [3].

Among various semiconductor metal oxides, TiO_2 , ZnO , NiO and CuO have been extensively investigated because of their attractive optical, electrical and catalytic properties. TiO_2 and ZnO are well-known wide band-gap semiconductors with excellent photocatalytic activity, whereas NiO and CuO are p-type semiconductors exhibiting superior visible-light absorption characteristics. Among them, cupric oxide has attracted significant attention due to its narrow band-gap (1.2–2.1 eV), high absorption coefficient, chemical stability, non-toxicity and low cost [4, 5]. Owing to these properties, CuO nanoparticles (NPs) have been widely explored for applications in photocatalysis, sensing, solar energy conversion, Li-ion batteries and optoelectronic devices [6, 7]. Furthermore, CuO nanostructures can be synthesized using various techniques, including sol-gel, hydrothermal, micro-wave assisted thermal decomposition and co-precipitation methods, enabling effective control over their structural and functional properties [8-10].

Zirconium dioxide (ZrO_2) is an important ceramic oxide that has attracted considerable interest due to its excellent thermal stability, high mechanical strength, chemical inertness, and wide band gap. Depending on temperature, dopant type and dopant concentration, ZrO_2 can exist in monoclinic, tetragonal and cubic polymorphic phases, each exhibiting distinct structural and functional characteristics [11-17]. Among these, tetragonal ZrO_2 has received particular attention because of its enhanced mechanical and optical properties. Owing to its superior physicochemical characteristics, ZrO_2 has been widely employed in catalysts, oxygen sensors, fuel cells, thermal barrier coating, biomedical implants and optical devices [13-15].

Among CuO -based nanostructures, CuO/ZrO_2 NCs have attracted considerable attention due to the synergistic interaction between the narrow band-gap CuO and wide band-gap ZrO_2 phases [18]. The incorporation of ZrO_2 can improve the dispersion, stability and interfacial characteristics of CuO , thereby influencing the structural, optical and catalytic properties of the composite system [19]. Consequently, CuO/ZrO_2 NCs have been extensively investigated for photocatalysis, gas sensing, environmental remediation and related functional applications. Previous studies have demonstrated that the physicochemical properties of CuO/ZrO_2 composites are strongly influenced by phase composition, crystallite size, defect concentration and interfacial interactions between the constituent oxides [20]. However, most reported investigations have primarily focused on catalytic performance and morphological characteristics, whereas detailed studies correlating phase evolution, microstructural modifications, lattice strain relaxation and luminescence behaviour remain limited.

In the present work, pure CuO , pure ZrO_2 NPs and CuO/ZrO_2 NCs were synthesized via hydrothermal route. The hydrothermal method was adopted owing to its simplicity with controlled morphology [21, 22]. Structural, microstructural and optical properties were systematically investigated using X-ray diffraction, Williamson–Hall analysis, scanning electron microscopy, energy-dispersive X-ray analysis, Fourier transform infrared spectroscopy, diffuse reflectance spectroscopy, and photoluminescence spectroscopy, while crystal structures were visualized using VESTA software. Particular emphasis was placed on understanding the influence of CuO incorporation on phase evolution, crystallite growth, lattice strain and optical response in the ZrO_2 matrix. The study establishes correlation between phase stabilization, microstructural modification and luminescence behaviour in CuO/ZrO_2 NCs.

2. Experimental:

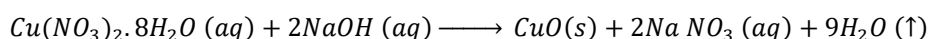
2.1. Materials:

All the chemicals used for the preparation of CuO/ZrO₂ nanocomposite (NC) including copper nitrate octahydrate (Cu(NO₃)₂·8H₂O), zirconium oxychloride octahydrate (ZrOCl₂·8H₂O), sodium hydroxide (NaOH) and ethanol (C₂H₆O) were analytical reagent grade (purity >99%) and were purchased from Merck chemicals, Mumbai India. Deionized water was used for sample preparation and dilutions. All glass vessels and crucibles used in this study were thoroughly acid-washed to remove impurities and ensure cleanliness.

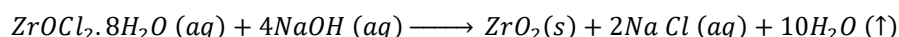
2.2. Synthesis of CuO/ZrO₂ nanocomposite:

Initially, 3.32 g of copper nitrate octahydrate (Cu(NO₃)₂·8H₂O) was dissolved in 20 mL of deionized water and stirred magnetically at room temperature. Simultaneously, 6.67 g of zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) was dissolved in 20 mL of deionized water, and 20 mL of ethanol was added to this solution. The zirconium precursor solution was then added to the copper precursor solution under constant stirring to form a light blue-coloured mixture. This mixture was stirred for 30 min, and the solution pH was adjusted to 6 using 0.5 M NaOH solution. Subsequently, the resulting solution was stirred at room temperature for 24 h and then transferred into a 150 mL Teflon-lined stainless-steel autoclave. The autoclave was maintained at 150 °C for 16 h under self-generated pressure. After cooling to room temperature, the obtained product was washed several times with distilled water and ethanol to remove impurities. The washed product was dried in an oven at 100 °C for 3 h and the dried material was ground into a fine powder for further characterization. Figure 1 shows the flow chart for the preparation of CuO/ZrO₂ NC.

For comparison, pure CuO and pure ZrO₂ NPs were synthesized by the same hydrothermal route using their respective precursors. In both cases, the pH was adjusted to 6 using 0.5 M NaOH, and the resulting suspensions were subjected to identical hydrothermal conditions as described above for the CuO/ZrO₂ NC. The obtained precipitates were washed thoroughly with distilled water and ethanol, dried at 100 °C for 3 hours, and gently grinded in agate mortar to obtain fine black CuO and white ZrO₂ powders, respectively. The stoichiometric balanced equations for the formation of CuO NPs are



For the formation of ZrO₂ is



3. Characterization Techniques:

The crystal structure of the synthesized NPs and NC was characterized using powder X-ray diffraction (XRD, Bruker D8) with Cu K_α radiation (λ = 1.5406 Å) over the 2θ range of 20°–80° [23]. Diffraction data were further processed using X'Pert Pro-software to determine crystallite size and phase composition. The Fourier transform infrared (FTIR) spectra were recorded in the wavenumber range 400 – 4000 cm⁻¹ using a Nicolet Magna-550 spectrometer. The morphology and elemental composition of the CuO/ZrO₂ NC were examined using a TESCAN VEGA3 LMU scanning electron microscope equipped with an EDX detector and operated at an accelerating voltage 15 kV. The particle size was analyzed by using the open-source ImageJ tool. The UV-Vis diffuse reflectance spectra were recorded using a Shimadzu UV-Vis spectrophotometer to investigate the optical properties of the synthesized samples. The crystal structure of NPs and NC was visualized by using open-source VESTA software. The photoluminescence (PL) spectra were recorded using a Perkin Elmer LS-55 spectrofluorometer operated at room temperature.

4. Results and Discussion:

4.1. Structural Properties:

4.1.1. X-ray diffraction

Figure 2(a) and (b) show that the XRD patterns of hydrothermally synthesized CuO, ZrO₂ NPS and CuO/ZrO₂ NC. The XRD pattern of CuO NPs confirms the formation of single phase monoclinic CuO with lattice parameter values of $a = 4.58 \text{ \AA}$, $b = 3.49 \text{ \AA}$, $c = 5.51 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, and $\beta = 96.75^\circ$. The diffraction peaks observed at $2\theta = 32.99^\circ, 36.00^\circ, 37.03^\circ, 39.23^\circ, 42.89^\circ, 49.26^\circ, 53.98^\circ, 58.71^\circ, 62.01^\circ, 66.59^\circ, 68.50^\circ, 72.96^\circ$, and 75.52° corresponding to the (110), (11 $\bar{1}$), (111), (200), (11 $\bar{2}$), (20 $\bar{2}$), (202), (11 $\bar{3}$), (310), (220), (311), (22 $\bar{2}$) lattice planes respectively. The peak positions and relative intensities are in good agreement with the standard JCPDS file No. 00-048-1548, confirming the formation of phase pure monoclinic CuO [24].

The XRD pattern of pure ZrO₂ NPs reveals the formation of monoclinic phase zirconia with lattice parameters of $a = 5.05 \text{ \AA}$, $b = 5.38 \text{ \AA}$ and $c = 5.28 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, and $\beta = 98.54^\circ$. Characteristic peaks located at $2\theta \approx 23.71^\circ, 28.21^\circ, 31.22^\circ, 34.29^\circ, 49.53^\circ, 54.85^\circ$ are indexed to the (011), ($\bar{1}11$), (111), (020), ($\bar{2}12$), (202), lattice planes, respectively. Zirconium oxide generally exists in three polymorphic forms, namely monoclinic (m-ZrO₂), tetragonal (t-ZrO₂) and cubic (c-ZrO₂), among which monoclinic phase is thermodynamically stable at low temperature, whereas the tetragonal and cubic are quite stable at elevated temperatures. The obtained XRD pattern agrees well with JCPDS Card No. 96-810-4265 and confirms the formation of monoclinic ZrO₂ [25].

Now the XRD patterns of CuO/ZrO₂ NC display both monoclinic and tetragonal phases of ZrO₂ in addition to a monoclinic phase of CuO. The strong peaks at $2\theta \approx 36.3^\circ, 47.7^\circ, 52.5^\circ$ and 58.7° are assigned to (002), ($\bar{1}12$), (020) and (202) planes of the monoclinic structures of CuO respectively. These peaks are in good agreement with the standard XRD data of JCPDS card no: 96-410-5686. The other characteristic peaks identified at nearly $2\theta \approx 29.7^\circ, 34.1^\circ, 50.1^\circ$ and 59.6° are assigned due to (101), (110), (200) and (211) plane of the tetragonal phase of ZrO₂. These peaks are well in agreement with JCPDS card number: 17-0923. The peaks further, emerged at about nearly $2\theta \approx 24.2^\circ, 28.9^\circ, 31.3^\circ, 45.4^\circ, 51.4^\circ$ and 56.7° are assigned to the (111), ($\bar{1}11$), (111) ($\bar{1}21$), ($\bar{2}02$) and (311) planes due to the monoclinic phase of ZrO₂, which are well in line with the peaks mentioned in the standard JCPDS card number 96-210-8454. Lattice parameters, Axes of symmetry and volume of unit cell of CuO, ZrO₂ NPs and CuO/ZrO₂ NC were presented in Table 1.

The monoclinic phase fraction (X_m) of ZrO₂ was estimated using the Garvie–Nicholson relation [26] (Eq-1) from the integrated intensities (I) of the characteristic monoclinic (-111) and (111) reflections at $2\theta \approx 28.9^\circ$ and 31.3° , together with the isolated tetragonal (101) reflection at $2\theta \approx 29.7^\circ$. The monoclinic volume fraction (V_m) was subsequently calculated using the Toraya corrections [27] (Eq. 2):

$$X_m = \frac{I_m(-111) + I_m(111)}{I_m(-111) + I_m(111) + I_t(101)} \quad \text{----- (1)}$$

Where m, t stands for monoclinic and tetragonal phases, respectively.

$$V_m = \frac{1.311 X_m}{1 + 0.311 X_m} \quad \text{----- (2)}$$

The calculated monoclinic volume fraction was found to be 72.69 %, indicating that m-ZrO₂ remained the dominant polymorph in the CuO/ZrO₂ NC. Compared with pure ZrO₂, the CuO/ZrO₂ NC exhibits a reduced monoclinic phase fraction together with partial stabilization of the tetragonal ZrO₂ phase. This behavior may be associated with interfacial strain, lattice mismatch, and interfacial interactions arising from the formation of the CuO/ZrO₂ heterojunctions.

The average crystallite size and lattice strain of the synthesized samples were evaluated using the Debye–Scherrer equation (Eq. 3) [28] and the Stokes–Wilson equation (Eq. 4) [29], respectively.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{-----(3)}$$

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad \text{-----(4)}$$

Where D is the average crystallite size, λ is the wavelength of the X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg diffraction angle. The average crystallite sizes of CuO and ZrO₂ were found to be 14.20 nm and 8.38 nm, respectively. The Williamson-Hall (WH) method was further employed to determine the crystallite size and lattice strain from the intercept and slope of the linear fit using Eq. (5). The calculated parameters are summarized in Table 2, and corresponding WH plots are presented in Figure 3.

$$\beta \cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin\theta \quad \text{-----(5)}$$

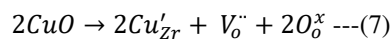
Furthermore, the dislocation density (δ) was calculated from crystallite size using the Williamson- Smallman equation (Eq. 6)

$$\delta = \frac{1}{D^2} \quad \text{-----(6)}$$

Upon hydrothermal synthesis, the crystallite size of the CuO/ZrO₂ NC increased to ~ 38nm compared with those of the individual CuO and ZrO₂ NPs, suggesting enhanced crystal growth during composite formation [29]. This

increase may be associated with interfacial diffusion and improved crystallinity resulting from the intimate contact between the two oxide phases. Furthermore, the XRD results reveal the coexistence of monoclinic and tetragonal ZrO₂ phases, indicating partial stabilization of the tetragonal ZrO₂ phase in the CuO/ZrO₂ NC. In pure zirconia, the monoclinic-to-tetragonal phase transformation is accompanied by significant lattice strain and volume change, which restrict crystallite growth [30, 31]. Therefore, the incorporation of CuO during hydrothermal synthesis is expected to influence the phase stability of ZrO₂ through interfacial interactions and strain relaxation.

A possible mechanism reported in the literature involves the substitution of Cu²⁺ ions at Zr⁴⁺ lattice sites, resulting in charge compensation through the formation of oxygen vacancies [32, 33]. This defect reaction can be represented using Kroeger-Vink notation as:



where Cu'_{Zr} represents a Cu ion occupying a Zr⁴⁺ site, V_o'' denotes an oxygen vacancy with an effective double positive charge, and O_o^x represents a lattice oxygen ion at its regular crystallographic site. The partial stabilization of the tetragonal phase is accompanied by reduced lattice strain and dislocation density, as evidenced by the Williamson-Hall analysis. The resulting strain relaxation facilitates grain-boundary migration during hydrothermal synthesis, leading to enhanced crystallite growth in the CuO/ZrO₂ NC compared with the individual oxide NPs.

4.1.2. SEM with EDAX:

The SEM micrograph of the CuO sample (Figure 4(a)) reveals irregularly shaped particles with pronounced agglomeration, forming densely packed secondary clusters rather than isolated primary NPs. The particles exhibit a rough and granular surface, indicating that each secondary particle consists of numerous smaller crystallites. ImageJ analysis estimated an average particle size ~980 nm, which is considerably larger than the average crystallite size (~14 nm) obtained from XRD analysis. This significant difference indicates that the observed particles are polycrystalline agglomerates formed through the assembly of multiple nanocrystallites.

Such agglomeration -driven growth is a characteristic feature of transition metal oxide nanomaterials synthesized via hydrothermal methods and has been widely reported in the literature [34-36].

The SEM micrograph of the ZrO_2 sample (Figure 4(b)) exhibits irregular to quasi-spherical particles with rough surfaces and non-uniform outlines. No anisotropic structures such as rods, plates or elongated structures are observed, suggesting predominantly isotropic crystal growth during hydrothermal synthesis. Similar to CuO , the ZrO_2 particles are strongly agglomerated into large secondary clusters composed of numerous nanocrystallites. ImageJ analysis yielded an average particle size of ~ 900 nm, which is substantially larger than the XRD crystallite size (~ 8 nm), confirming the agglomerated polycrystalline nature of the particles. The exclusive presence of the monoclinic phase observed by XRD indicates that, in the absence of stabilizing species, hydrothermal synthesis favours the thermodynamically stable monoclinic ZrO_2 phase at room temperature [37].

The SEM micrograph of the CuO/ZrO_2 NC (Figure 4(c)) reveals a heterogeneous cauliflower-like morphology composed of irregular to quasi-spherical agglomerates decorated with fine nodular features. The rough surface texture reflects the intimate assembly of CuO and ZrO_2 nanocrystallites into hierarchical secondary particles without the formation of anisotropic structures, indicating isotropic growth behaviour. ImageJ analysis shows a broad particle-size distribution ranging from approximately 200 to 1400 nm, with an average particle size of about 800 nm. As in the individual oxide samples, the particle size is significantly larger than the crystallite size obtained from XRD, confirming that the observed particles are secondary agglomerates consisting of multiple nanocrystallites. The reduced particle size of the composite compared with pure CuO and ZrO_2 suggests that the incorporation of CuO influences the growth behaviour during hydrothermal synthesis. Moreover, the absence of observable phase segregation indicates uniform dispersion of the constituent phases, consistent with the heterostructure formation inferred from XRD analysis.

Figure 5 presents the EDAX spectra of (a) CuO , (b) ZrO_2 and (c) CuO/ZrO_2 NC together with their corresponding elemental compositions. The EDAX spectra confirm the presence of Cu and O in CuO , Zr and O in ZrO_2 , and Cu, Zr and O in the CuO/ZrO_2 NC without detectable impurity elements, demonstrating the high purity of the synthesized materials. Elemental mapping further reveals a homogenous spatial distribution of Cu, Zr and O throughout the NC, indicating uniform dispersion of constituent phases. These observations are in good agreement with the XRD results and further support the successful formation of a homogeneous CuO/ZrO_2 NC.

4.1.3. Crystal Structure Visualization and Coordination Analysis

Figure 6(a) presents the VESTA visualization of the monoclinic CuO crystal structure generated from CIF file number 9016326 obtained from the Crystallography Open Database (COD). The lattice parameters (a , b , c and β) were replaced with the experimentally determined values obtained from XRD analysis, whereas the space group and atomic fractional coordinates were retained from the reference CIF file. The resulting model was used solely for crystal structural visualization and coordination analysis. The VESTA output contains 22 atoms, 24 bonds and six coordination polyhedra within the displayed unit cell. Each Cu^{2+} ion is coordinated by six oxygen atoms in a distorted CuO_6 octahedron consisting of four shorter equatorial Cu-O bonds and two elongated axial Cu-O bonds, characteristic of the Jahn-Teller distorted elongated octahedral (4+2) coordination environment. The distorted CuO_6 coordination environment is therefore useful for understanding the relationship between the local atomic arrangement and the crystallographic structure of monoclinic CuO .

Figure 6(b) presents the VESTA visualization of monoclinic ZrO_2 (space group $\text{P2}_1/\text{C}$), generated from CIF file No. 2108453 obtained from the COD. The lattice parameters were replaced with the experimentally

determined values obtained from XRD analysis, whereas the space group and atomic fractional coordinates were retained from the reference CIF file. The VESTA output contains 24 atoms, 28 bonds and four coordination polyhedra within displayed unit cell. Each Zr^{4+} ion is coordinated by seven oxygen atoms, forming a distorted ZrO_7 polyhedron consisting of four relatively shorter and three longer Zr-O bonds. The unequal Zr-O bond lengths reflect the low-symmetry coordination environment characteristic of monoclinic zirconia and are consistent with the crystal structure identified by XRD. The distorted ZrO_7 coordination environment provides a structural basis for understanding the local atomic arrangement and crystallographic characteristics of the monoclinic ZrO_2 phase.

Figure 7 presents the VESTA visualization of the constituent phases in the CuO/ZrO_2 NC, generated using CIF file No. 9016326 for monoclinic CuO, No. 2108453 for monoclinic ZrO_2 , and No. 1525705 for tetragonal ZrO_2 . The lattice parameters of the individual phases were replaced with the experimentally determined values obtained from XRD analysis (Table 1), while the corresponding space groups and atomic fractional coordinates were retained from the reference CIF files. The structural models illustrate the coexistence of monoclinic CuO with distorted CuO_6 coordination, the predominant monoclinic ZrO_2 phase containing distorted ZrO_7 polyhedra and a minor tetragonal ZrO_2 phase characterized by ZrO_8 coordination polyhedra. The coexistence of these coordination environment is consistent with the phase composition determined from XRD analysis and supports the partial stabilization of the tetragonal ZrO_2 phase in the CuO/ZrO_2 NC. The structural mismatch between the distorted CuO_6 octahedra and ZrO_7 polyhedra may generate localized interfacial distortion, which could contribute to the stabilization of the ZrO_8 coordination environments associated with tetragonal ZrO_2 . These structural models provide a visualization of the local coordination environments and complement the crystallographic phase analysis obtained from XRD, thereby offering an atomic-scale perspective on the structural evolution of the CuO/ZrO_2 NC.

Figure 8 Schematically illustrates the multiscale structural evolution of the CuO/ZrO_2 nanocomposite by correlating the atomic-scale coordination environments (VESTA), Crystallographic phase evolution (XRD) and nanocrystalline agglomerated morphology (SEM). The Schematic provides a conceptual framework for understanding the observed structure-property relationships.

4.2. Optical properties:

4.2.1. Fourier Transform Infrared Spectroscopy (FTIR):

Figure 9 compares the FTIR spectra of CuO, ZrO_2 and CuO/ZrO_2 NC recorded in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$. The spectra were analysed to identify the characteristic metal-oxygen vibrations, surface functional groups and structural changes associated with the formation of the CuO/ZrO_2 NC.

The FTIR spectra of CuO NPs exhibits a strong absorption band at $\sim 590\text{ cm}^{-1}$, corresponding to the characteristic Cu-O stretching vibration of the monoclinic CuO. A weak shoulder observed near 550 cm^{-1} is assigned to the Cu-O bending vibration [38]. The appearance of this weak bending mode is consistent with the local lattice distortion associated with the Jahn-Teller distorted CuO_6 coordination environment identified from the crystal structure analysis. Bands observed at ~ 1352 and 835 cm^{-1} are attributed to C-O stretching vibrations arising from surface-absorbed carbonate species, which may originate from atmospheric CO_2 absorption or residual precursor species [39]. The absorption band in the $1400\text{--}1600\text{ cm}^{-1}$ region corresponds to the H-O-H bending vibrations of absorbed water molecule [40], whereas the broad band extending from ~ 2500 to 3200 cm^{-1} is assigned to O-H stretching vibrations of surface hydroxyl groups and physically absorbed water molecules

[41]. The broad and low-intensity nature of this band indicates the presence of surface hydroxylation and absorbed moisture, which are commonly observed in hydrothermally synthesized CuO NPs.

The FTIR spectra of ZrO₂ NPs exhibits strong absorption band around 600cm⁻¹, corresponding to the characteristic Zr-O stretching vibrations, whereas the weak band near 825cm⁻¹ is assigned to the Zr-O-Zr bending vibration [42]. These low-wave number absorption bands confirm the formation of zirconia framework and are consistent with the monoclinic ZrO₂ phase identified by XRD. The absorption band centered at ~1654 cm⁻¹ is attributed to the H-O-H bending vibration of absorbed water molecules, while the broad absorption band observed in the 3200 to 3400 cm⁻¹ region corresponds to the O-H stretching vibrations of surface hydroxyl groups and physically absorbed moisture. The presence of these hydroxyl-related bands is characteristic of hydrothermally synthesized zirconia and indicates surface hydroxylation arising from exposure to atmospheric moisture. The FTIR observations are consistent with the structural model established from XRD and VESTA.

The FTIR spectrum of the CuO/ZrO₂ NC exhibits significant broadening of the low-wavenumber region together with shoulder features, arising from the overlap of the characteristic Cu-O and Zr-O lattice vibrations following composite formation. Such spectral broadening may be associated with variations in bond lengths and local coordination environments resulting from the coexistence of CuO₆, ZrO₇ and ZrO₈ structural units, as illustrated by the VESTA analysis [43]. In addition, C-O (~ 1380 cm⁻¹), H-O-H (~ 1680cm⁻¹) and broad O-H (~2500 – 3000 cm⁻¹) bands indicate the absorption of atmospheric CO₂ and moisture on the NC surface. These observations are consistent with the lattice-strain evolution obtained from the Williamson-Hall analysis and support the successful formation of the CuO/ZrO₂ NC.

4.2.2. UV-Vis Diffuse Reflectance spectra (DRS):

Figure 10 shows the UV-Vis diffuse reflectance spectra (DRS) of CuO, ZrO₂ NPs and CuO/ZrO₂ NC recorded in the wavelength range 300-1200 nm at room temperature. The optical band gap was determined from Kubelka-Munk function $F(R)$, by extrapolating the linear portion of the $[F(R)hv]^n$ versus hv plots, and the calculated values are summarized in Table 4. According to the Kubelka-Munk [44], the relation between Kubelka-Munk function $F(R)$ and absorption coefficient K is given by Eq. (8)

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \text{-----(8)}$$

Where ‘S’ is the scattering coefficient. The optical band gaps evaluated from Kubelka approach for CuO NPs is about 2.44 eV, for ZrO₂ NPs is about 4.04 eV, and for CuO/ZrO₂ NC is about 3.64 eV. The obtained band gaps for CuO and ZrO₂ NPs are in good agreement with findings reported in literature [45-46]. Pure ZrO₂ NPs exhibit strong absorption in UV region with high reflectance throughout the visible range, characteristic of a wide band gap oxide. In contrast, CuO NPs show intense absorption extending across visible region, indicating their narrow band gap semiconducting nature. The CuO/ZrO₂ NC shows an intermediate band gap of 3.64 eV, which is significantly reduced compared to pure ZrO₂ and higher than that of CuO. The intermediate band gap of the CuO/ZrO₂ NC indicates electronic interaction between CuO and ZrO₂ and is consistent with the heterostructure formation inferred from XRD and SEM analysis. The observed reduction in the optical band gap may be associated with several factors. The intimate contact between CuO and ZrO₂ in the NC can modify the interfacial electronic structure, while lattice mismatch and the accompanying strain may influence the electronic band structure. In addition, interfacial defects and oxygen-vacancy related states, within the band gap, thereby contributing to the observed band gap reduction.

4.2.3. Photoluminescence Spectra

Figure 11(a) shows the room temperature photoluminescence (PL) spectrum of CuO NPs excited at 350 nm. The spectrum exhibits a broad emission band extending from ~380 –480 nm. Gaussian deconvolution resolves the broad emission into three components centered at approximately 400 nm (3.10 eV), 422 nm (2.94 eV) and 461 nm (2.67 eV) respectively [47]. These emissions are attributed to defect-assisted radiative recombination rather than direct band-to-band transitions, considering the much narrower optical band gap of CuO determined from DRS analysis. The emission at ~400 nm is assigned to defect-related electronic transitions, whereas the peaks at ~422 and ~461 nm are associated with oxygen-vacancy related defect states and deep-level recombination involving $\text{Cu}^{2+}/\text{Cu}^+$ defect centers. The observed PL behaviour therefore indicates that intrinsic lattice defects play an important role in the radiative recombination process of hydrothermally synthesized CuO NPs.

Figure 11(b) shows the room temperature PL spectrum of ZrO_2 NPs excited at 350 nm. The broad visible emission band was deconvoluted using Gaussian fitting into two components centered at ~428 nm (2.90 eV) and 479 nm (2.59 eV). Considering the wide optical band gap of ZrO_2 (4.80 eV) obtained from DRS analysis, no near band-edge emission is expected in the visible region, indicating that the observed emission originates from defect-assisted radiative recombination. The emission at ~428 nm is attributed to oxygen-vacancy related defect centers, whereas the lower energy emission at ~479 nm is associated with deep-level defect states arising from oxygen-vacancy clusters and surface-related defects [48, 49]. These observations are consistent with the defect-rich nature of hydrothermally synthesized ZrO_2 and agree well with the monoclinic phase identified by XRD.

Figure 11(c) shows the room temperature PL spectrum of the CuO/ ZrO_2 NC excited at 350 nm. The broad emission was resolved into four Gaussian components centered at ~403, 427, 454 and 456 nm. The emission at ~403 nm is attributed to defect-related electronic transitions associated with CuO, whereas the ~427 nm peak originated from oxygen-vacancy related defect centers in ZrO_2 . The additional emissions at ~454 nm and ~456 nm was assigned to deep level defect states that may arise from oxygen-vacancy related defects and local interfacial electronic states formed during composite synthesis. Compared with the individual CuO and ZrO_2 NPs, the CuO/ ZrO_2 NC exhibits an additional emission component while retaining the characteristic emission features of both constituent oxides. The appearance of this additional emission, without significant spectral broadening, suggests the formation of new radiative recombination centers associated with composite formation rather than extensive structural disorder.

The PL behavior of the CuO/ ZrO_2 NC is consistent with the structural and optical characteristics revealed by XRD, FTIR, VESTA and DRS analysis. The additional defect related emission and reduced optical band gap suggest modified defect-assisted radiative recombination following composite formation, making the NC a promising candidate for visible-light driven photocatalytic and optoelectronic applications.

5. Conclusions:

In this study, CuO, ZrO_2 NPs and CuO/ ZrO_2 NC were successfully synthesized via the hydrothermal route and systematically characterized using XRD, SEM, EDAX, VESTA, FTIR, DRS and PL analyses. XRD revealed the coexistence of monoclinic CuO with predominantly monoclinic ZrO_2 together with partial stabilization of tetragonal ZrO_2 phase in the CuO/ ZrO_2 NC. Williamson-Hall analysis confirmed the nanocrystalline nature of all synthesized samples, while SEM observations showed that the NPs formed agglomerated secondary particles composed of multiple nanocrystallites. EDAX confirmed the high purity and homogenous elemental distribution of the constituent elements, whereas VESTA visualization provided atomic-scale insight into the coordination environments of CuO_6 , ZrO_7 and ZrO_8 polyhedra. FTIR, DRS and PL analyses demonstrated that composite

formation modifies the local bonding environment, optical band gap, and defect-assisted radiative recombination behaviour compared with the individual oxide NPs. These complementary structural and optical characteristics indicate that the CuO/ZrO₂ NC is a promising material for visible-light driven photocatalytic, gas sensing and optoelectronic applications.

6. Acknowledgments:

The Authors express their heartfelt thanks to "Nanotechnology Research Laboratory", Department of Freshman Engineering, Prasad. V. Potluri. Siddhartha Institute of Technology, Vijayawada, Andhra Pradesh. For their support by accommodate a platform for synthesis facility for the purpose of accomplish the ongoing research activity. The authors convey their deep sense of gratitude to Siddhartha Academy of General and Technical Education for giving the financial support and the uplifting in persistent the research work.

7. References:

- [1] Supriya S, Jeon SM, Naik R, Rout CS (2026) Xenon for next-generation photodetectors: Recent advances, challenges, and future perspectives. *Adv Mater Technol* 11:e02573. <https://doi.org/10.1002/admt.202502573>
- [2] Zaib, S., Ahmad, B., & Iqbal, S. Nanocrystal Architectures for Enhanced Optoelectronic Properties: A Paradigm Shift in Energy Harvesting and Storage. *Spectrum of Engineering Sciences*, 4(6) 717–771 (2026). <https://doi.org/10.5281/zenodo.20604697>
- [3] Dixit, C. K., Srivastava, S., Singh, P., & Pandey, A. K. Analysis of Finite Strain Theory for Modeling a New EOS for Nanomaterials. *Nano-Structures & Nano-Objects*, 38 101121 (2024). <https://doi.org/10.1016/j.nanoso.2024.101121>
- [4] Khalaji, A. D., Pazhand, Z., Kiani, K., Macheek, P., Jarosova, M., & Mazandarani, R. CuO Nanoparticles: Preparation, Characterization, Optical Properties, and Antibacterial Activities. *J. Mater. Sci.: Mater. Electron.*, 31 11949–11954 (2020). <https://doi.org/10.1007/s10854-020-03749-1>
- [5] Sahooli, M., Sabbaghi, S., & Saboori, R. Synthesis and Characterization of Mono Sized CuO Nanoparticles. *Mater. Lett.*, 81 169–172 (2012). <https://doi.org/10.1016/j.matlet.2012.04.148>
- [6] Ighalo, J. O., Sagboye, P. A., Umenweke, G., Ajala, O. J., Omoarukhe, F. O., Adeyanju, C. A. C. T., Ogunniyi, S., & Adeniyi, A. G. CuO Nanoparticles (CuO NPs) for Water Treatment: A Review of Recent Advances. *Environ. Nanotechnol. Monit. Manag.*, 15 100443 (2021). <https://doi.org/10.1016/j.enmm.2021.100443>
- [7] Phiwdang, K., Suphankij, S., Mekprasart, W., & Pecharapa, W. Synthesis of CuO Nanoparticles by Precipitation Method Using Different Precursors. *Energy Procedia*, 34 740–745 (2013). <https://doi.org/10.1016/j.egypro.2013.06.808>
- [8] Dagher, S., Haik, Y., Ayesh, A. I., & Tit, N. Synthesis and Optical Properties of Colloidal CuO Nanoparticles. *J. Lumin.*, 151 149–154 (2014). <https://doi.org/10.1016/j.jlumin.2014.02.015>
- [9] Parekh, Z. R., Chaki, S. H., Hirpara, A. B., Patel, G. H., Kannaujiya, R. M., Khimani, A. J., & Deshpande, M. P. CuO Nanoparticles – Synthesis by Wet Precipitation Technique and Its Characterization. *Physica B: Condens. Matter*, 610 412950 (2021). <https://doi.org/10.1016/j.physb.2021.412950>
- [10] Dhineshababu, N., Rajendran, N., Nithyavathy, N., & Vetumperumal, R. Study of Structural and Optical Properties of CuO Nanoparticles. *Appl. Nanosci.*, 6 933–939 (2016). <https://doi.org/10.1007/s13204-015-0503-4>

- [11] Reddy, C. V., Reddy, I. N., Shim, J., Cho, M., Yoo, K., & Kim, D. Excellent Visible-Light Driven Photocatalyst of CuO–TiO₂ Nanocomposites for Organic Dye Degradation and Hydrogen Evolution. *Ceram. Int.*, 44 6940–6948 (2018). <https://doi.org/10.1016/j.ceramint.2018.01.060>
- [12] Fathima, J. B., Pugazhendhi, A., & Venis, R. Synthesis and Characterization of CuO Nanoparticles for Antibacterial Activity Using *Tridax procumbens* Leaf Extract. *Microb. Pathog.*, 110 245–251 (2017). <https://doi.org/10.1016/j.micpath.2017.06.065>
- [13] Reyes-Acosta, M. A., García-González, L., Moreno, K. J., Espinosa-Pesqueira, M. E., & Martínez-Juárez, J. Structural, Optical and Magnetic Properties of CuO Nanoparticles Prepared by Solution Combustion Method. *J. Alloys Compd.*, 643 S150–S158 (2015). <https://doi.org/10.1016/j.jallcom.2014.12.222>
- [14] Ordóñez, F., Chejne, F., Pabón, E., & Cacia, K. Synthesis of ZrO₂ Nanoparticles and Effect of Surfactant on Dispersion and Stability. *Ceram. Int.*, 46 11970–11977 (2020). <https://doi.org/10.1016/j.ceramint.2020.01.236>
- [15] Wang, Y., Hua, H., Liu, H., Zhu, M., & Zhu, X. X. Biodegradable Polymeric Nanoparticles for Biomedical Applications: Recent Advances in Design and Surface Engineering. *ACS Appl. Bio Mater.*, 3 5300–5309 (2020). <https://doi.org/10.1021/acsabm.0c00682>
- [16] Anandan, K., Rajesh, K., & Rajendran, V. Enhanced Optical Properties of Spherical Zirconia (ZrO₂) Nanoparticles Synthesized via the Facile Various Solvents Mediated Solvothermal Process. *J. Mater. Sci.: Mater. Electron.*, 28 17321–17330 (2017). <https://doi.org/10.1007/s10854-017-7664-1>
- [17] Pandit, N. A., & Ahmad, T. ZrO₂/CeO₂-Heterostructured Nanocomposites for Enhanced Carbon Monoxide Gas Sensing. *ACS Appl. Nano Mater.*, 6(9) 7299–7309 (2023). <https://doi.org/10.1021/acsanm.3c00412>
- [18] Viruthagiri, G., Gopinathan, E., Shanmugam, N., & Gobi, R. Synthesis and Characterization of ZrO₂–CuO Co-Doped Ceria Nanoparticles via Chemical Precipitation Method. *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.*, 131 556–563 (2014). <https://doi.org/10.1016/j.saa.2014.04.117>
- [19] Hernández Battez, A., González, R., Viesca, J. L., Fernández, J. E., Díaz Fernández, J. M., Machado, A., Chou, R., & Riba, J. CuO, ZrO₂ and ZnO Nanoparticles as Antiwear Additive in Oil Lubricants. *Wear*, 265(3–4) 422–428 (2008). <https://doi.org/10.1016/j.wear.2007.11.013>
- [20] Renuka L, Anantharaju KS, Vidya YS, Nagaswarupa HP, Prashantha SC, Sharma SC, Nagabhushana H, Darshan GP (2017) A simple combustion method for the synthesis of multi-functional ZrO₂/CuO nanocomposites: Excellent performance as sunlight photocatalysts and enhanced latent fingerprint detection. *Appl Catal B Environ* 210:97–115. <https://doi.org/10.1016/j.apcatb.2017.03.055>
- [21] Shailaja NR, Arulmozhi M, Balraj B, Siva C, et al (2024) *Corallocarpus epigaeus* mediated synthesis of ZnO/CuO integrated ZrO₂ nanoparticles for enhanced in-vitro antibacterial, antifungal and antidiabetic activities. *Int J Intell Comput Sci*. <https://doi.org/10.1016/j.ijics.2023.100991>
- [22] Azhar S, Ahmad KS, Abrahams I, et al (2023) Synthesis of phyto-mediated CuO–ZrO₂ nanocomposite and investigation of their role as electrode material for supercapacitor and water splitting studies. *J Mater Res* 38:4937–4950. <https://doi.org/10.1557/s43578-023-01204-5>
- [23] Ali MH, Azad MAK, Khan KA, Rahman MO, Chakma U, Kumar A (2023) Analysis of crystallographic structures and properties of silver nanoparticles synthesized using PKL extract and nanoscale characterization techniques. *ACS Omega* 8(31):28133–28142. <https://doi.org/10.1021/acsomega.3c01261>

- [24] Okpara EC, Ogunjinmi OE, Oyewo OA, Fayemi OE, Onwudiwe DC (2021) Green synthesis of copper oxide nanoparticles using extracts of *Solanum macrocarpon* fruit and their redox responses on SPAu electrode. *Heliyon* 7(12):e08571. <https://doi.org/10.1016/j.heliyon.2021.e08571>
- [25] Xia W, Wang F, Mu X, Chen K, et al (2017) Remarkably enhanced selectivity for conversion of ethanol to propylene over ZrO₂ catalysts. *Fuel Process Technol* 167:351–358. <https://doi.org/10.1016/j.fuproc.2017.06.002>
- [26] Garvie RC, Nicholson PS (1972) Phase analysis in zirconia systems. *J Am Ceram Soc* 55(6):303–305. <https://doi.org/10.1111/j.1151-2916.1972.tb11290.x>
- [27] Toraya H, Yoshimura M, Somiya S (1984) Calibration curve for quantitative analysis of the monoclinic–tetragonal ZrO₂ system by X-ray diffraction. *J Am Ceram Soc* 67(6):C119–C121. <https://doi.org/10.1111/j.1151-2916.1984.tb19715.x>
- [28] Manjushree SG, Adarakatti PS, Udayakumar V (2021) Engineering of CuO/ZrO₂ nanocomposite-based electrochemical sensor for the selective detection of hydrogen peroxide. *Ionics* 27:5309–5322. <https://doi.org/10.1007/s11581-021-04243-2>
- [29] Kumari N, Sareen S, Verma M, Sharma S, Sharma A, Sohal HS, Mehta SK, Park J, Mutreja V (2022) Zirconia-based nanomaterials: Recent developments in synthesis and applications. *Nanoscale Adv* 4(20):4210–4236. <https://doi.org/10.1039/d2na00367h>
- [30] Li H, Qian W, Zhang Z, Wang S, Chen Y, Zhang F, Hou Z, Gao G, Zhao Q, Zhan H (2025) The phase stability of t-ZrO₂ realized by grain size at cryogenic temperature in ZrO₂/TiO₂ composite. *Mater Des* 255:112741. <https://doi.org/10.1016/j.matdes.2024.112741>
- [31] Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr A* 32:751–767. <https://doi.org/10.1107/S0567739476001551>
- [32] Chen C, Ruan C, Zhan Y, Lin X, Zheng Q, Wei K (2014) The significant role of oxygen vacancy in Cu/ZrO₂ catalyst for enhancing water-gas-shift performance. *Int J Hydrogen Energy* 39(1):317–324. <https://doi.org/10.1016/j.ijhydene.2013.10.074>
- [33] Aidhy DS, Rawat K (2021) Coupling between interfacial strain and oxygen vacancies at complex-oxides interfaces. *J Appl Phys* 129:171102. <https://doi.org/10.1063/5.0049001>
- [34] Saravanakumar D, Abou Oualid H, Brahmi Y, Ayeshamariam A, Karunanithy M, Mohamed Saleem A, Kaviyarasu K, Sivaranjani S, Jayachandran M (2019) Synthesis and characterization of CuO/ZnO/CNTs thin films on copper substrate and its photocatalytic applications. *OpenNano* 4:100025. <https://doi.org/10.1016/j.onano.2018.11.001>
- [35] Devi AB, Moirangthem DS, Talukdar NC, Devi MD, Singh NR, Luwang MN (2014) Novel synthesis and characterization of CuO nanomaterials: Biological applications. *Chin Chem Lett* 25(12):1615–1619. <https://doi.org/10.1016/j.ccllet.2014.07.014>
- [36] Živković A, Solsona-Delgado V, van der Linden B, de Leeuw NH, Melián-Cabrera I (2023) Molecular-level understanding of interfacial carbonates in stabilizing CuO–ZnO(Al₂O₃) catalysts. *J Catal* 425:406–421. <https://doi.org/10.1016/j.jcat.2023.06.032>
- [37] Akter SS, Babu MH, Imae SM, Hossain MK, Chowdhury FI (2025) Combined DFT and experimental study of CuO and Ni–CuO nanoparticles: Structural characterization, photocatalytic degradation, and antimicrobial activities. *RSC Adv* 15(49):41479–41496. <https://doi.org/10.1039/d5ra06284e>

- [38] Chitori AK, Mir A, Shah MA (2023) A review of ZrO₂ nanoparticles applications and recent advancements. *Ceram Int* 49(20):32343–32358. <https://doi.org/10.1016/j.ceramint.2023.06.296>
- [39] Jalil AT, Alquraby HE, Al Qurabiy, et al (2021) CuO/ZrO₂ nanocomposites: Facile synthesis, characterization and photocatalytic degradation of tetracycline antibiotic. *J Nanostruct* 11(2):333–346. <https://doi.org/10.22052/JNS.2021.02.014>
- [40] Ganga BG, Santhosh PN (2014) Manipulating aggregation of CuO nanoparticles: Correlation between morphology and optical properties. *J Alloys Compd* 612:456–464. <https://doi.org/10.1016/j.jallcom.2014.05.171>
- [41] Hosseini SG, Sheikhpour A, Keshavarz MH, Tavangar S (2016) The effect of metal oxide particle size on the thermal behavior and ignition kinetic of Mg–CuO thermite mixture. *Thermochim Acta* 626:1–8. <https://doi.org/10.1016/j.tca.2016.01.005>
- [42] Khan R, Inam MA, Akram M, Uddin A, Khan S, Yeon IT (2019) Effect of dissolved organic matter on agglomeration and removal of CuO nanoparticles by coagulation. *Processes* 7(7):455. <https://doi.org/10.3390/pr7070455>
- [43] Vollath D, Fischer FD, Hagelstein M, et al (2006) Phases and phase transformations in nanocrystalline ZrO₂. *J Nanopart Res* 8:1003–1016. <https://doi.org/10.1007/s11051-006-9116-3>
- [44] Simmons EL (1975) Diffuse reflectance spectroscopy: A comparison of the theories. *Appl Opt* 14(6):1380–1386. <https://doi.org/10.1364/AO.14.001380>
- [45] Akter J, Sapkota KP, Hanif MA, Islam MA, Abbas HG, Hahn JR (2021) Kinetically controlled selective synthesis of Cu₂O and CuO nanoparticles toward enhanced degradation of methylene blue using ultraviolet and sun light. *Mater Sci Semicond Process* 123:105570. <https://doi.org/10.1016/j.mssp.2020.105570>
- [46] Keiteb AS, Saion E, Zakaria A, Soltani N (2016) Structural and optical properties of zirconia nanoparticles by thermal treatment synthesis. *J Nanomater* 2016:1913609. <https://doi.org/10.1155/2016/1913609>
- [47] Jamal M, Billah MM, Ayon SA (2023) Opto-structural and magnetic properties of fluorine doped CuO nanoparticles: An experimental study. *Ceram Int* 49(6):10107–10118. <https://doi.org/10.1016/j.ceramint.2022.11.194>
- [48] Kumari S, Sharma E, Verma J, Dalal J, Kumar A (2023) Structural and photoluminescence properties of Dy-doped nanocrystalline ZrO₂ for optoelectronics application. *Ceram Int* 49(12):20185–20192. <https://doi.org/10.1016/j.ceramint.2023.03.142>
- [49] Bauri J, Choudhary RB (2023) Thermal and electronic states of exfoliated gC₃N₄-based nanocomposite with ZrO₂ nanoparticles as a robust emissive layer. *Mater Sci Semicond Process* 154:107205. <https://doi.org/10.1016/j.mssp.2022.107205>

Figure 1. Flow chart for the preparation of CuO/ZrO₂ NC.

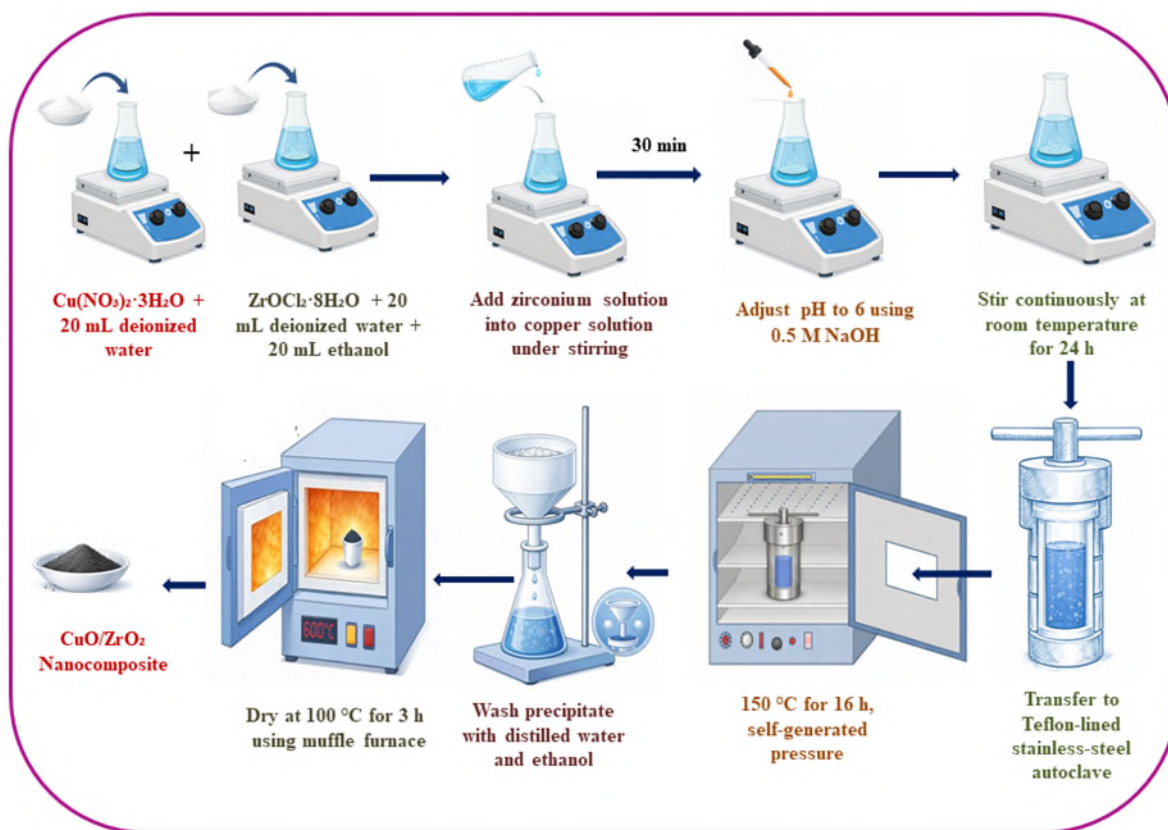


Figure 2(a). XRD patterns of synthesized CuO NP and ZrO₂ NP with JCPDS reference comparison.

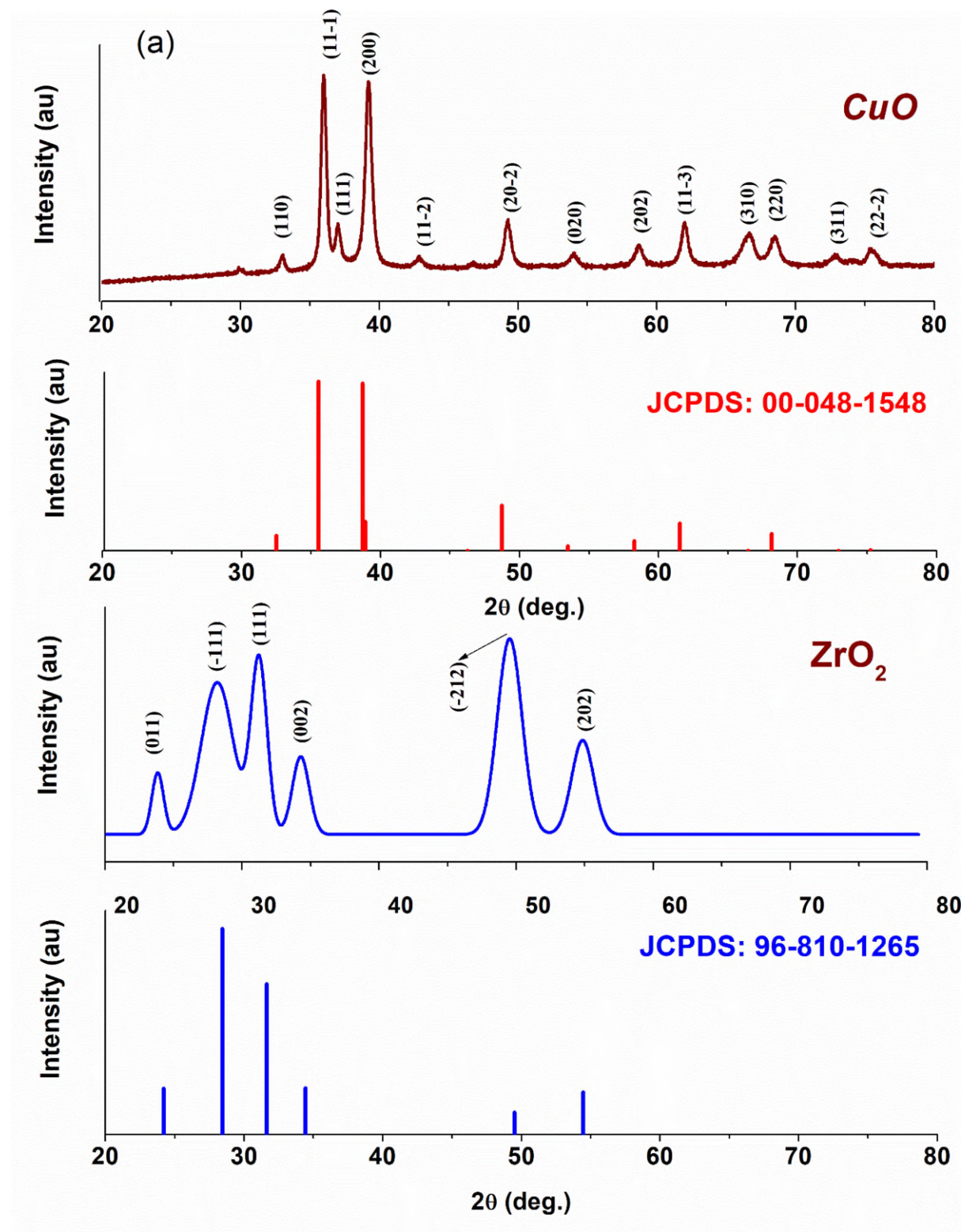


Figure 2(b). XRD patterns of synthesized CuO/ZrO₂ NC with JCPDS reference comparison

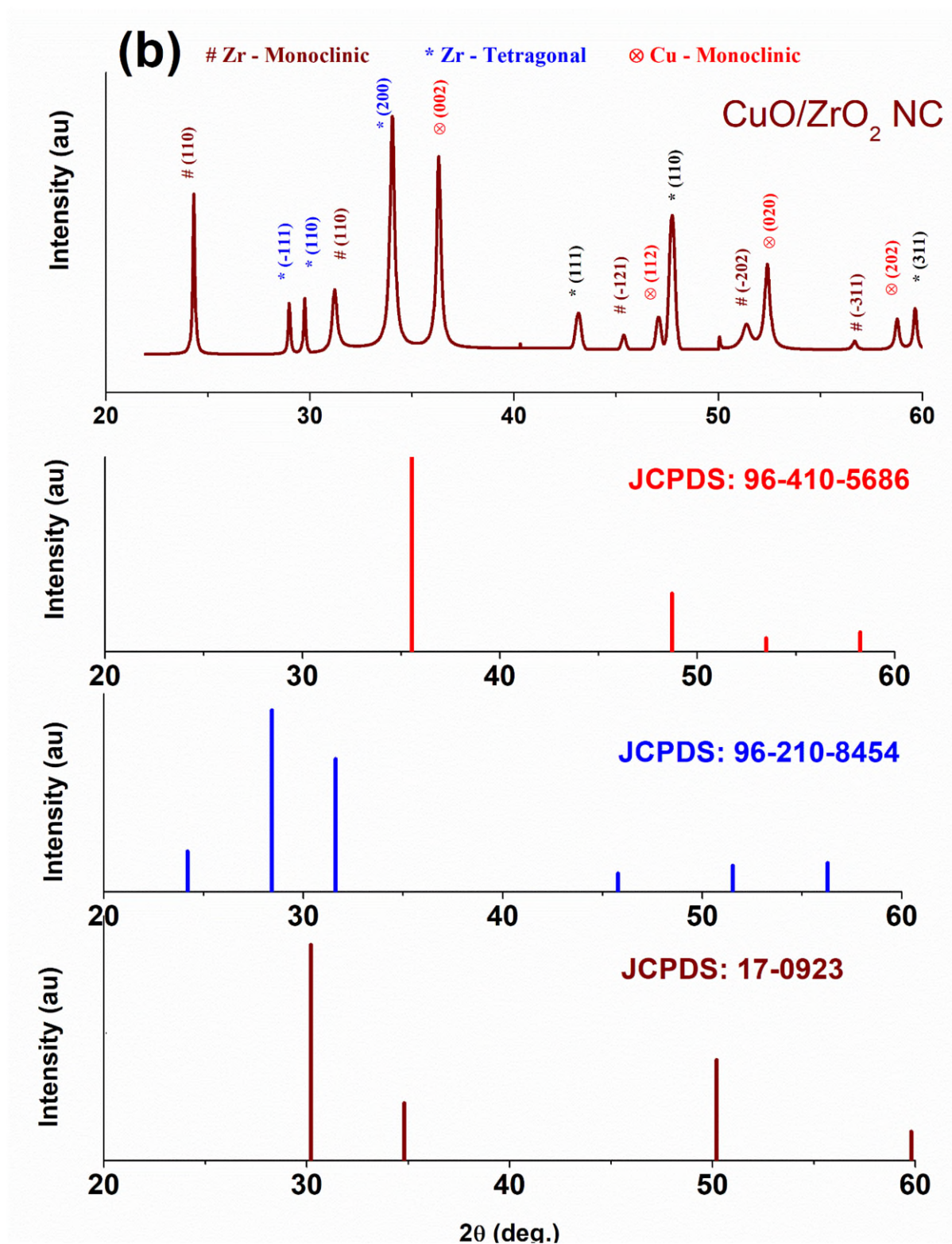


Figure 3. WH Plot of (a) CuO NP (b) ZrO₂ NP and (c) CuO/ZrO₂ NC.

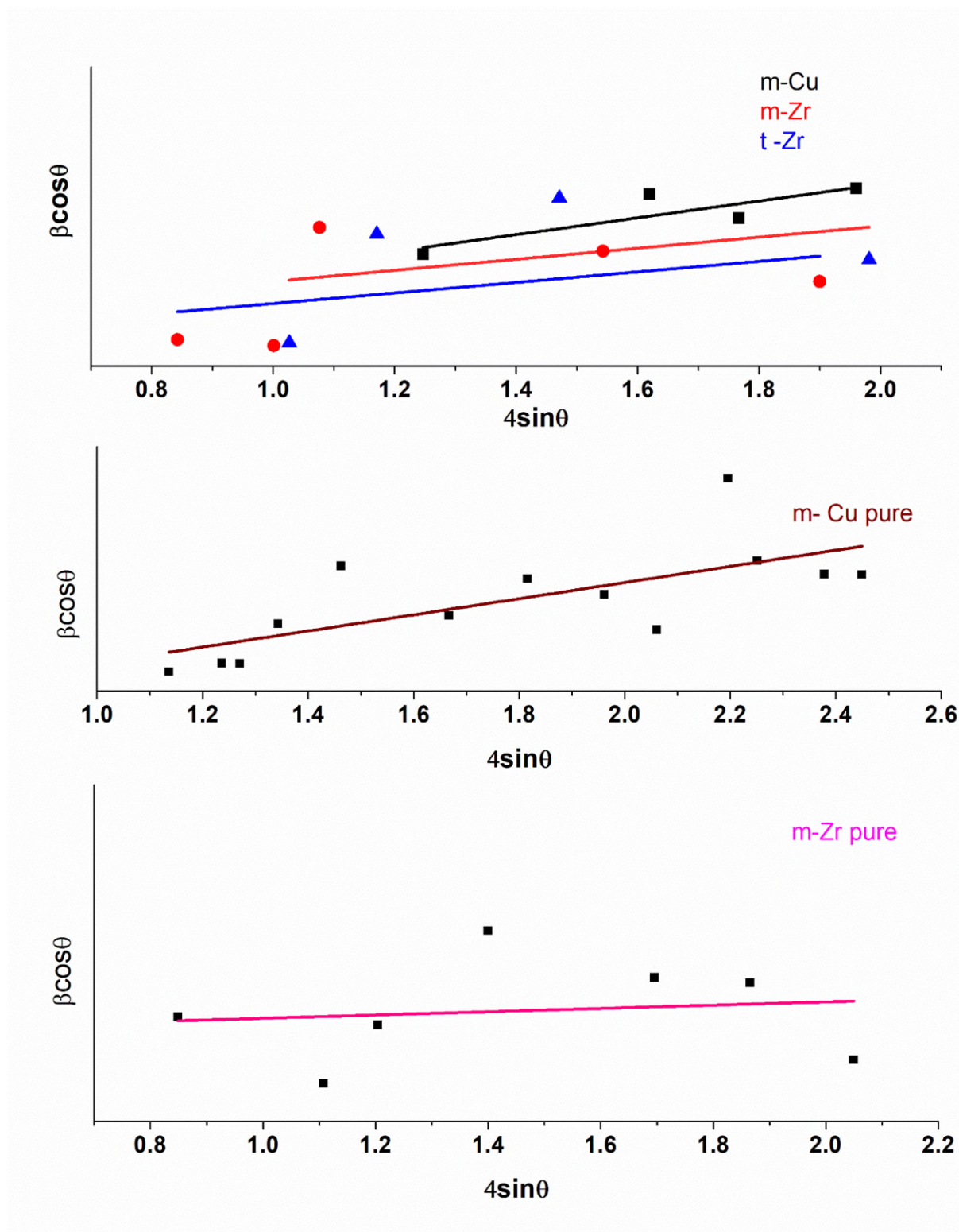


Figure 4. SEM micrograph of CuO, ZrO₂ NPs and CuO/ZrO₂ NC and particle size distribution fitted with Gaussian function.

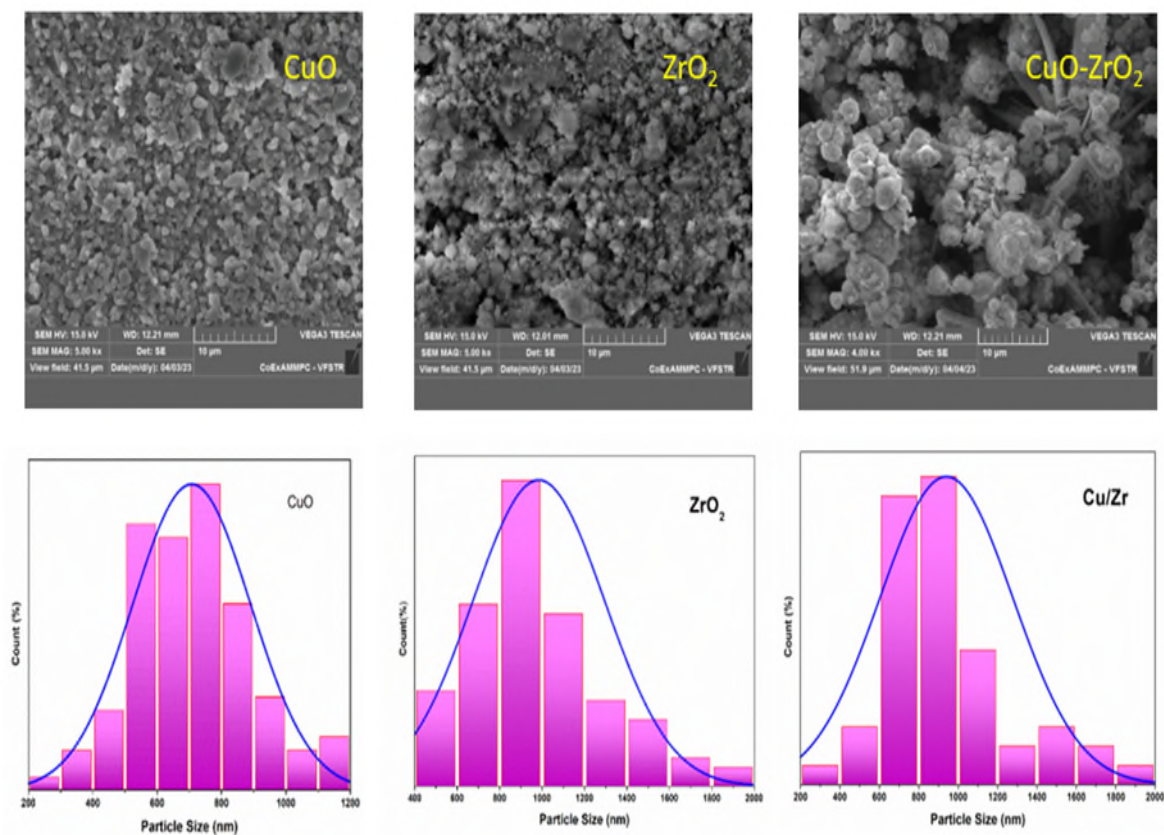


Figure 5. EDAX spectra and corresponding elemental composition of CuO, ZrO₂ NPs and CuO/ZrO₂ NC.

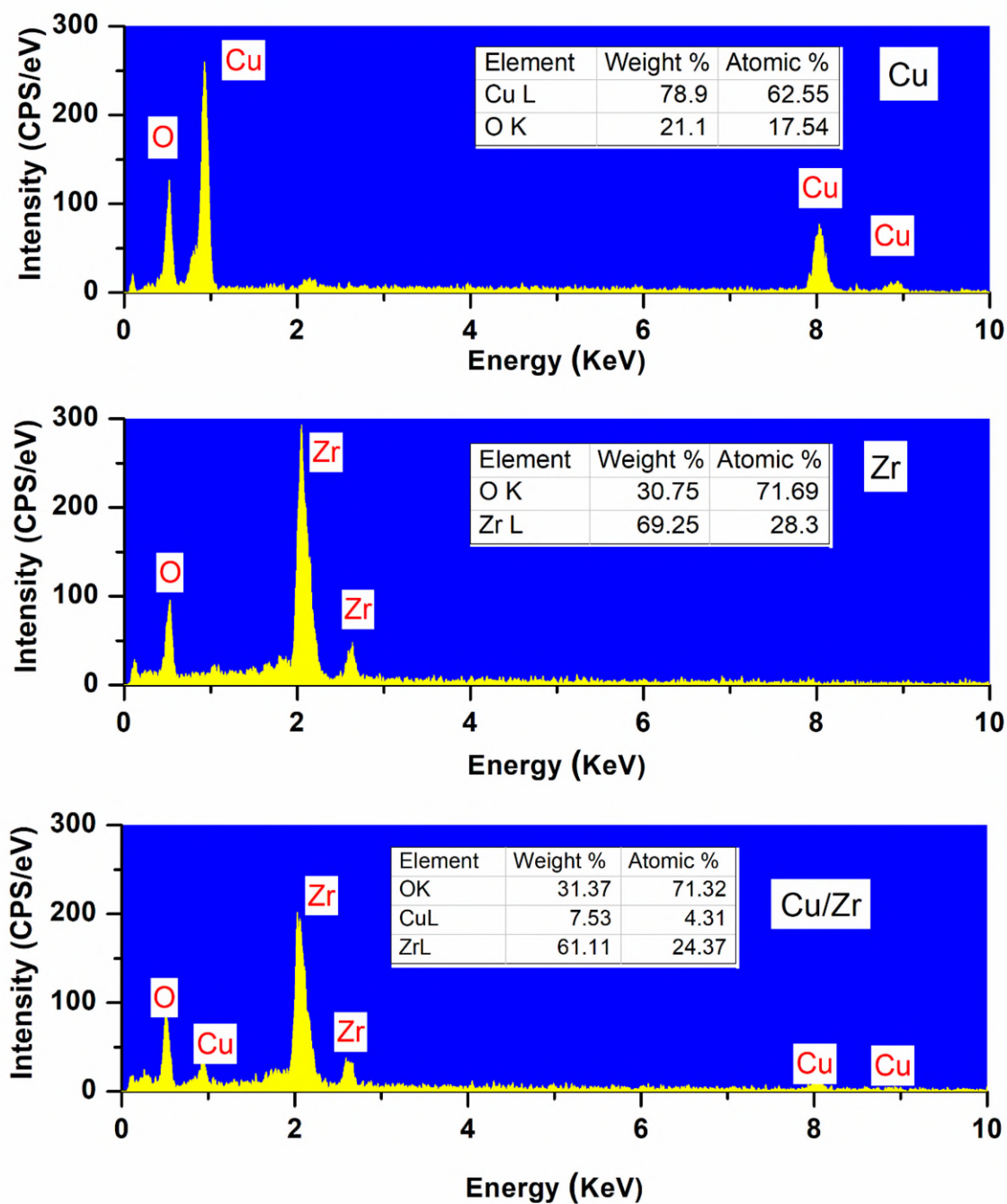


Figure 6. Crystal structures of (a) monoclinic CuO and (b) monoclinic ZrO₂ visualized ball-and-stick and polyhedral models (VESTA)

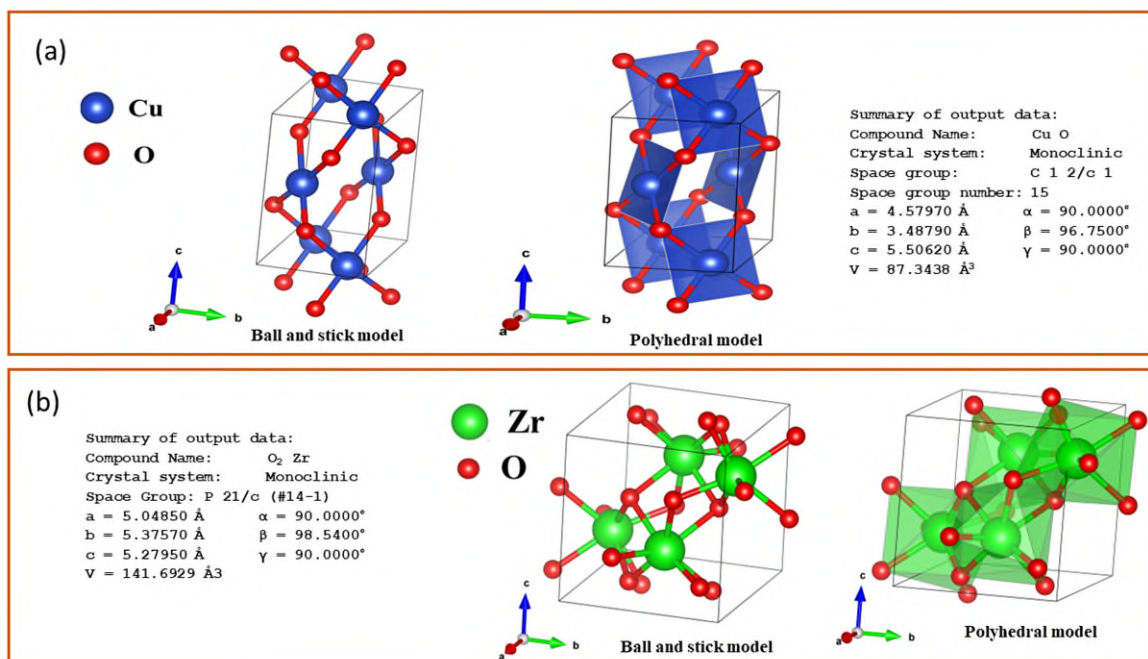


Figure 7. Crystal structure visualization of the individual and combined phases present in the CuO/ZrO₂ NC. Ball-and-Stick (top row) and polyhedral models (bottom row) using VESTA illustrate monoclinic CuO (m-CuO), monoclinic ZrO₂ (m-ZrO₂), tetragonal ZrO₂ (t-ZrO₂) and their co-existence.

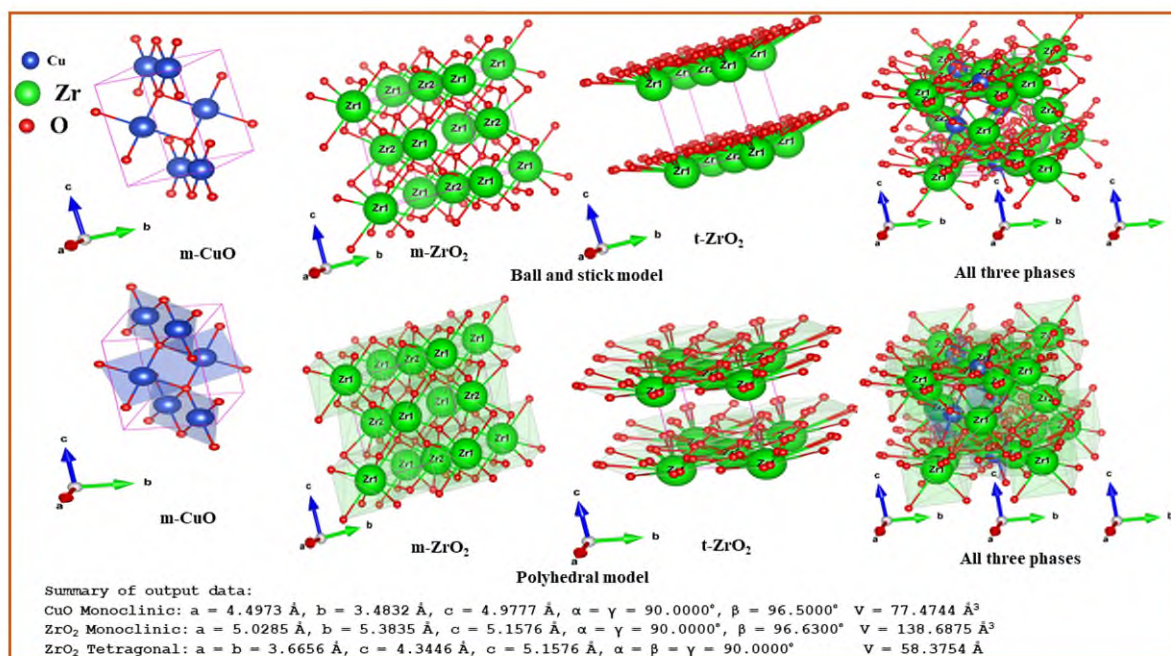


Figure 8. Multiscale structural correlation in CuO/ZrO₂ NC: Atomic Distortion, phase Evolution and morphology

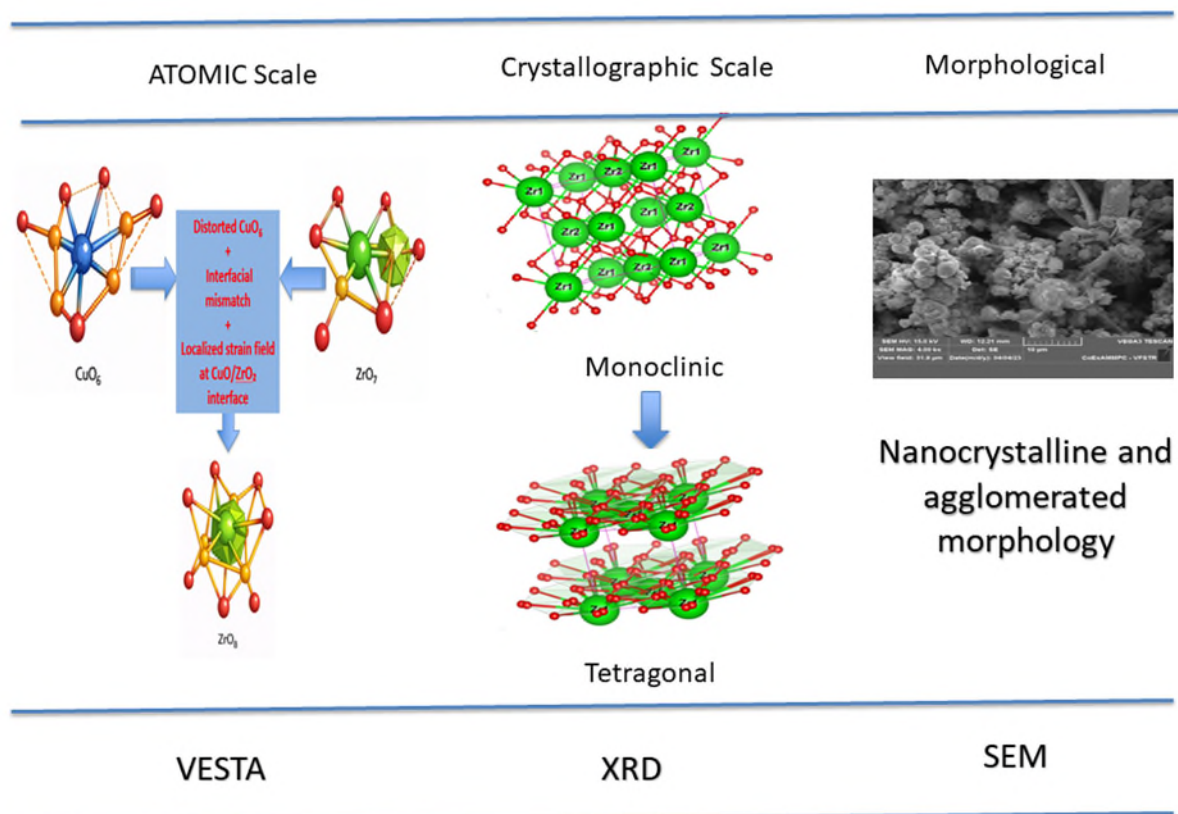


Figure 9. FTIR spectra of CuO, ZrO₂ NPs and CuO/ZrO₂ NC.

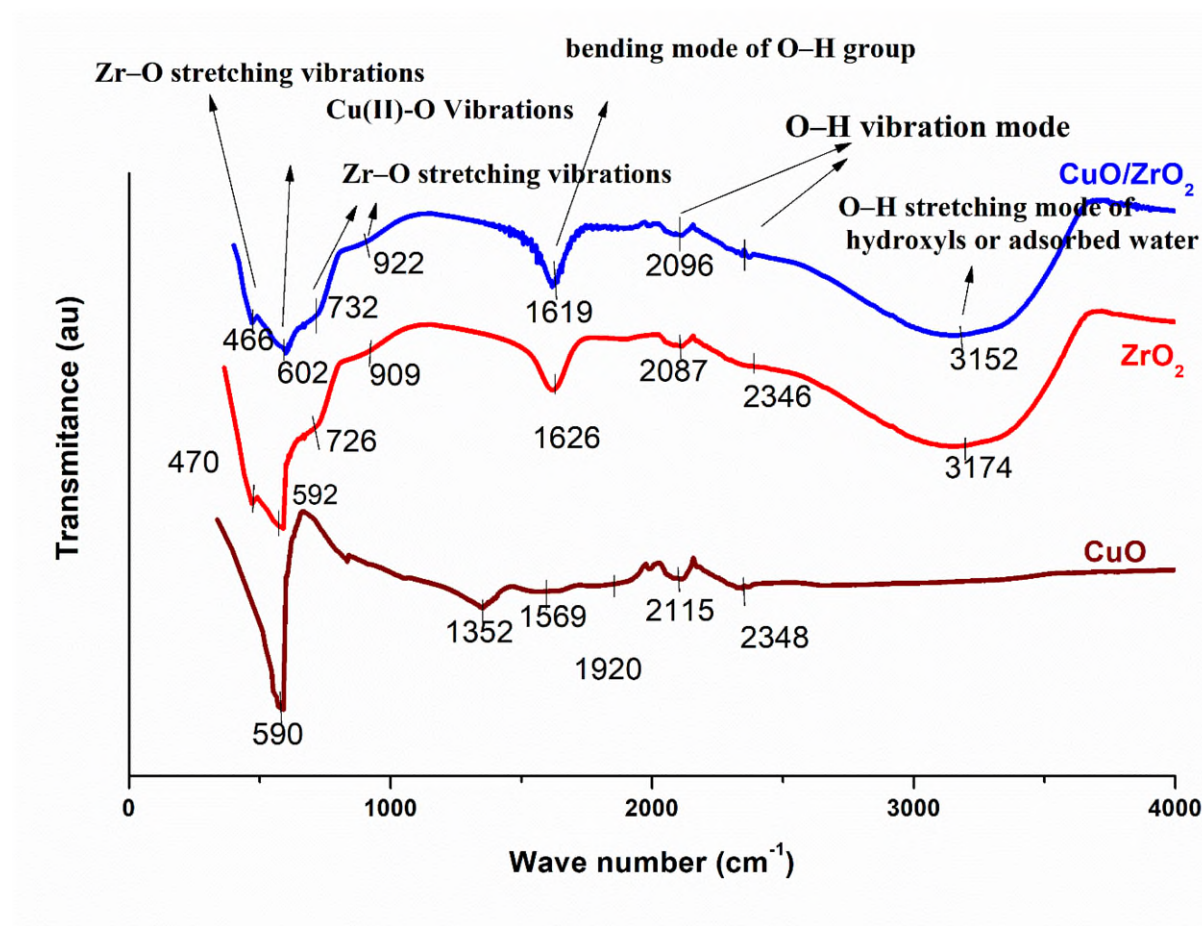


Figure 10. DRS spectra of Pure CuO, ZrO₂ NPs and CuO/ZrO₂ NC.

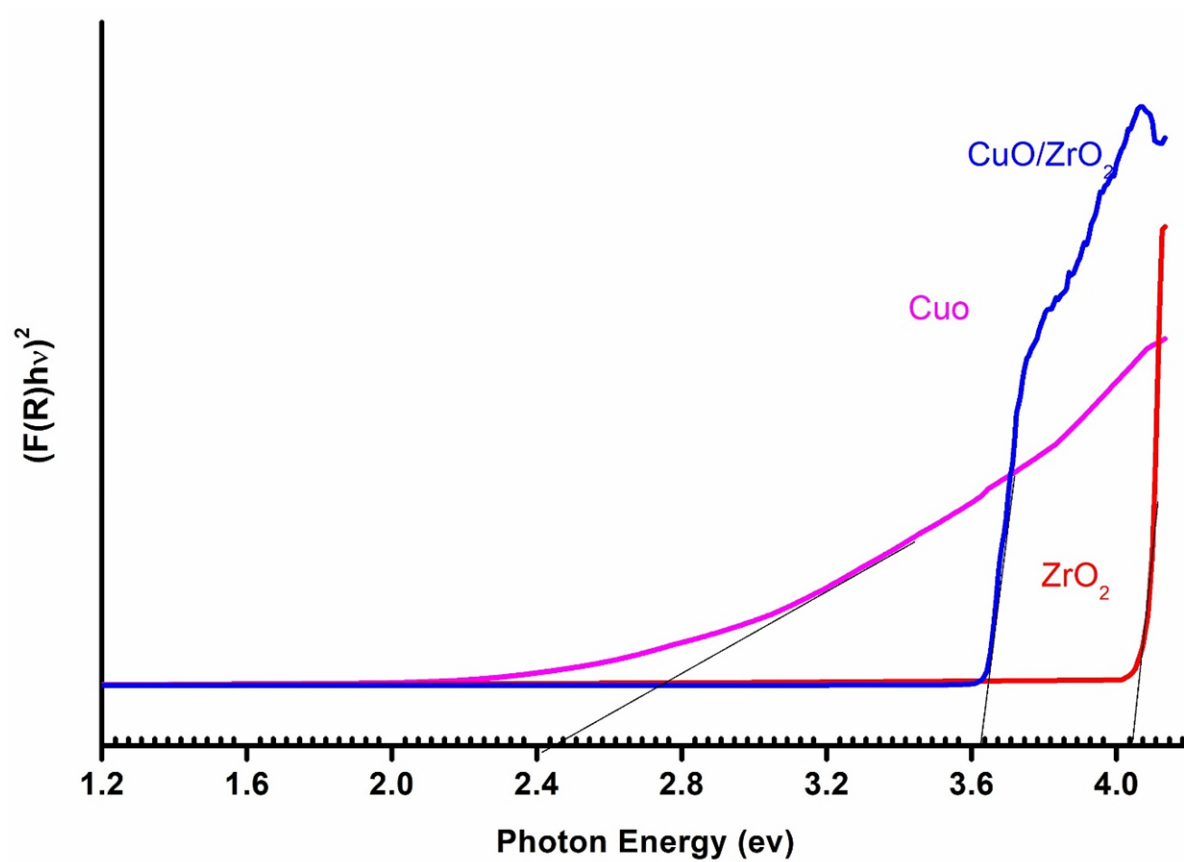


Figure 11. Photoluminescence of (a) CuO NP (b) ZrO₂ NP and (c) CuO/ZrO₂ NC.

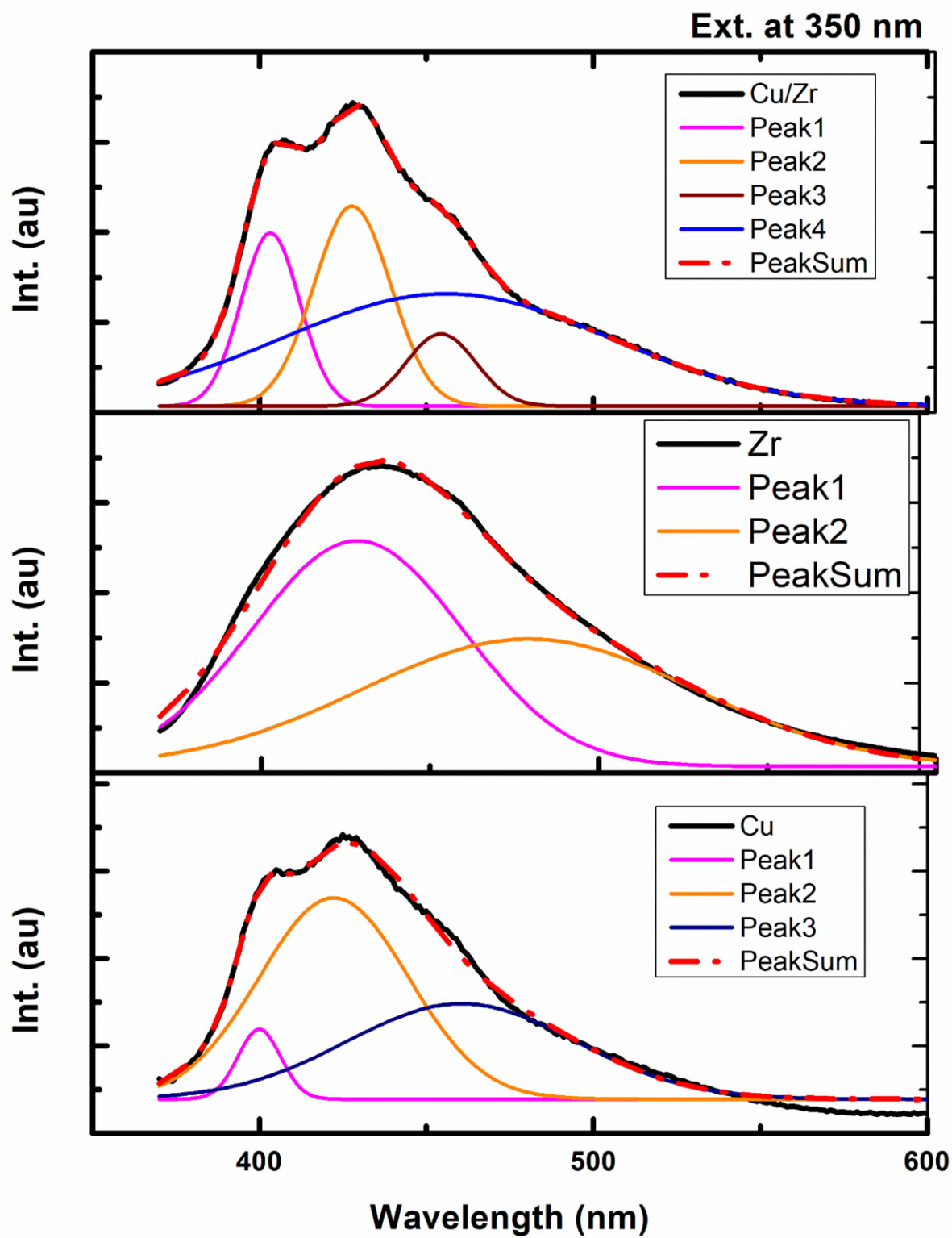


Table 1 Phase component, lattice parameters, Axes of symmetry and Volume of unit cell of CuO, ZrO₂ NP and CuO/ZrO₂ NC

Sample code	Phase of component	Lattice parameters (Å)			Volume of Unit cell (Å) ³	Axes of symmetry
		a	b	c	Mono. = $\sin\beta abc$ Tetragonal = a^2c	$\alpha=\beta=90^\circ$ and γ
Cu	Monoclinic	4.58	3.49	5.51	87.34	$\alpha=\gamma=90^\circ$, $\beta=96.75^\circ$
Zr	Monoclinic	5.05	5.37	5.28	141.59	$\alpha=\gamma=90^\circ$, $\beta=98.54^\circ$
Cu/Zr	CuO – Monoclinic	4.50	3.48	4.98	77.47	$\alpha=\gamma=90^\circ$, $\beta=96.50^\circ$
	ZrO ₂ – Monoclinic	5.03	5.38	5.16	138.68	$\alpha=\gamma=90^\circ$, $\beta=96.63^\circ$
	ZrO ₂ – Tetragonal	3.67	3.67	4.34	58.37	$\alpha=\beta=\gamma=90^\circ$

Table 2 Average crystal lattice size, lattice strain and dislocation density of CuO, ZrO₂ NP and CuO/ZrO₂ NC from Debye-Scherrer and W-H plot calculations

Sample Code	Crystallite size (nm)		Lattice strain (ϵ) $\times 10^{-4}$		Dislocation density (δ) ($\delta \times 10^{15} \text{ m}^{-2}$)	
	Scherer's	W-H plot	Scherer's	W-H plot	Scherer's	W-H plot
Cu	14.27	38.19	57.84	36.32	4.92	0.69
Zr	8.38	28.51	179.68	129.74	24.77	1.23
Cu/Zr						
Cu– mono.	33.08	75.76	26.95	18.00	0.91	0.17
Zr– mono.	43.67	80.61	33.02	11.42	0.52	0.15
Zr– tetra.	44.25	64.79	28.86	12.04	0.51	0.24

Table 3 Infrared Transmission spectra bands assignment and their relative positions in cm^{-1} of CuO, ZrO_2 NP and CuO/ ZrO_2 NC

Band Assignment	Band positions (cm^{-1})			Intensity
	CuO	ZrO_2	CuO/ ZrO_2	
Zr–O stretching vibrations	---	470	466	Strong intense
Cu(II)-O Vibrations	590	---	602	Strong intense
Zr–O stretching vibrations	---	726	732	Weak
		910	922	
Cu–O– Cu linkages	1350	---	—	Weak band
bending mode of O–H group	1569	1626	1619	Strong intense
or surface hydroxyls	1920			
O–H vibrations mode for	2015	2087	2096	Weak intense
CuO/ ZrO_2 nanoparticles.	2348	2346	2332	
O–H stretching mode of	---	3174	3152	Broad and intense
hydroxyls or adsorbed water				

Table 4 Optical band gap energies derived from UV-VIS DRS and emission band positions obtained from PL spectra of CuO, ZrO₂ NP and CuO/ZrO₂ NC

Code of Sample	Optical energy gap (eV)	PL peak position (nm)			
		Peak1	Peak 2	Peak 3	Peak 4
Cu NP	2.44	400	422	461	--
Zr NP	4.04	428	479	--	--
Cu/Zr NC	3.64	403	427	454	456

0

Figure Captions

1. Figure 1. Flow chart for the preparation of CuO/ZrO₂ NC
2. Figure 2(a). XRD patterns of synthesized CuO NP and ZrO₂ NP with JCPDS reference comparison
3. Figure 2(b). XRD patterns of synthesized CuO/ZrO₂ NC with JCPDS reference comparison
4. Figure 3. WH Plot of (a) CuO NP (b) ZrO₂ NP and (c) CuO/ZrO₂ NC
5. Figure 4. SEM micrograph of CuO, ZrO₂ NPs and CuO/ZrO₂ NC and particle size distribution fitted with Gaussian function
6. Figure 5. EDAX spectra and corresponding elemental composition of CuO, ZrO₂ NPs and CuO/ZrO₂ NC
7. Figure 6. Crystal structures of (a) monoclinic CuO and (b) monoclinic ZrO₂ visualized ball-and-stick and polyhedral models (VESTA)
8. Figure 7. Crystal structure visualization of the individual and combined phases present in the CuO/ZrO₂ NC. Ball-and-Stick (top row) and polyhedral models (bottom row) using VESTA illustrate monoclinic CuO (m-CuO), monoclinic ZrO₂ (m-ZrO₂), tetragonal ZrO₂ (t-ZrO₂) and their co-existence.
9. Figure 8. Multi scale structural correlation in CuO/ZrO₂ NC: Atomic Distortion, phase Evolution and morphology
10. Figure 9. FT–IR spectra of CuO, ZrO₂ NPs and CuO/ZrO₂ NC
11. Figure 10. DRS spectra of Pure CuO, ZrO₂ NPs and CuO/ZrO₂ NC.
12. Figure 11. Photoluminescence of (a) CuO NP (b) ZrO₂ NP and (c) CuO/ZrO₂ NC.

Table Captions

1. Table 1. Phase component, lattice parameters, Axes of symmetry and Volume of unit cell of CuO, ZrO₂ NP and CuO/ZrO₂ NC
2. Table 2. Average crystal lattice size, lattice strain and dislocation density of CuO, ZrO₂ NP and CuO/ZrO₂ NC from Debye-Scherrer and W-H plot calculations
3. Table 3. Infrared Transmission spectra bands assignment and their relative positions in cm⁻¹ of CuO, ZrO₂ NP and CuO/ZrO₂ NC
4. Table 4. Optical band gap energies derived from UV-VIS DRS and emission band positions obtained from PL spectra of CuO, ZrO₂ NP and CuO/ZrO₂ NC

