

Structure–Optical Property Correlation of Co-Doped TiO₂ and ZnO Nanofillers for Advanced Functional Composite Applications

Anil Kumar^{1,*}, Swati², Niharika³

Abstract

This study investigates the enhancement of the structural and optical properties of titanium dioxide (TiO₂) and zinc oxide (ZnO) nanoparticles through cobalt (Co) doping. Pristine TiO₂ and ZnO are widely studied metal oxides; however, their large band gaps and limited visible-light absorption restrict their performance in optoelectronic, photocatalytic, and environmental applications. Co doping is employed as an effective strategy to overcome these limitations by inducing band-gap narrowing, creating defect-related electronic states, and modifying the crystalline and morphological features of the host materials. TiO₂ and ZnO nanoparticles were synthesized using sol–gel and co-precipitation methods, respectively, allowing controlled dopant incorporation and uniform particle distribution. The successful substitution of Co ions into the TiO₂ and ZnO lattices was confirmed through comprehensive characterization techniques, including X-ray diffraction (XRD), UV–visible spectroscopy, Fourier-transform infrared spectroscopy (FTIR), and transmission electron microscopy (TEM). Structural analysis revealed that TiO₂ retained its anatase phase, while ZnO preserved its hexagonal wurtzite structure, indicating high phase stability even after doping. Optical studies demonstrated a noticeable red shift in absorption edges and enhanced visible-light absorption, attributed to Co-induced defect levels and altered electronic structures. Morphological analysis showed improved crystallinity and reduced particle agglomeration in the doped samples. Furthermore, Co-doped nanoparticles exhibited enhanced catalytic efficiency and structural robustness compared to their undoped counterparts. The results highlight the potential of Co-doped TiO₂ and ZnO as energy-efficient and environmentally friendly nanomaterials. In addition, these doped metal-oxide nanoparticles can function as effective Nano fillers in polymer and hybrid composite systems, significantly improving optical performance, photocatalytic activity, and environmental remediation efficiency.

Keywords: Cobalt doping, Titanium dioxide, Zinc oxide, Band gap reduction, Sol-gel synthesis, Photocatalysis.

*Author for Correspondence

Anil Kumar

¹Associate Professor, Department of Applied Science, Bharati Vidyapeeth's College of Engineering, New Delhi, India

²Assistant Professor, Department of Chemistry, Baba Mastnath University, Rohtak, Haryana, India

³Research Scholar, Department of Chemistry, Baba Mastnath University, Rohtak, Haryana, India

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INTRODUCTION

Metal oxide nanomaterials, particularly titanium dioxide (TiO₂) and zinc oxide (ZnO), are of significant interest due to their exceptional structural, optical, and electronic properties, making them ideal for applications in photocatalysis, optoelectronics, and environmental remediation. Despite their advantages, TiO₂ and ZnO face challenges such as wide band gaps and low visible light absorption. Cobalt (Co) doping has emerged as an effective strategy to address these issues by reducing the band gap, introducing defect states,

and modifying the crystalline structure, thus enhancing their photocatalytic and optoelectronic properties. This study explores the effects of Co doping in TiO₂ and ZnO, focusing on structural changes, band gap reduction, and improved charge carrier dynamics [3, 5]. Using metal dopants in TiO₂ alters its electronic structure so that it absorbs visible light as a result of introducing local energy levels within the band gap [27]. As a result, the crystalline structure, size of unit cells, and defect sites are also changed, all of which together determine the material's usefulness in being a catalyst and an optoelectronic device. Accordingly, due to its hexagonal wurtzite organisation and broad band gap, ZnO is regarded as very promising for detecting ultraviolet (UV) and for use in photocatalytic applications [1]. Nevertheless, using zinc selenide for processes involving visible light is still hard because its band gap energy is too high (around 3.3 eV). Replacing other atoms in silicon by cobalt ions could shrink the band gap and introduce extra defects, which make the material capable of absorbing visible light [10, 11]. It is important to control many factors, especially dopant amount, how the materials were created, and the annealing conditions, to obtain the desired changes in doped TiO₂ and ZnO nanomaterials. Most often, the sol-gel and co-precipitation methods are adopted because they are not expensive, are easy to perform, and allow for precise morphology and composition of nanostructures [6, 8]. They help incorporating dopants in the main lattice, which affects the lengths of the atoms, the strain in the material, and the number of defects, making it possible to modify the properties of the material. It has been found that adding cobalt to TiO₂ and ZnO causes clear differences in their structure, appearance, and light-related activities [24]. Information from XRD studies confirms that the doping process results in adjustments in the crystal structure and reveals that dopants are integrated in the host sample [12, 13]. No matter how you dope TiO₂, it keeps its anatase structure, while doping levels in ZnO do not change its wurtzite phase nor show signs of impurity [14, 15]. Co doping can be confirmed by UV-visible spectroscopy to cause a noticeable change in the band gap. With the addition of cobalt doping to TiO₂, the band gap narrows from 2.8 eV to 2.4 eV, making it simpler for the material to capture visible lighting [9, 11]. In a related way, ZnO's band gap decreases from 3.14 eV to 2.77 eV, and this is accompanied by a noticeable shift of the absorption edge to longer wavelengths. Researchers attribute it to sp-d exchange interaction happening between the Co d-electrons and the band electrons of ZnO [2, 21].

In addition, Co doping in TiO₂ and ZnO affects their properties of light interaction. Studies of PL have shown that defect passivation decreases emission peaks and more non-radiative pathways open up, which boosts the photoactivities of the material [18, 19]. It is also confirmed by FTIR spectroscopy that dopants cause defect levels and changes in the bond structures of the nanomaterials [22, 23]. The addition of metal cobalt to TiO₂ and ZnO gives a versatile approach for boosting their structure and light-related properties for advanced uses. This research focuses on the production, study of their features, and optimization of the material properties of Co-doped TiO₂ and ZnO nanoparticles by using the sol-gel and co-precipitation techniques. Analyzing the shapes, structures, and optical properties of such materials allows a clear picture of the main processes that improve their functions. Results in this paper have a strong potential for improving and developing nanomaterials aimed at catalysis, energy, and environmental purposes [7]. In recent years, metal-oxide nanoparticles such as TiO₂ and ZnO have been extensively used as functional fillers in polymer nanocomposites, coatings, membranes, and hybrid composite systems to improve UV shielding, photocatalytic self-cleaning behavior, and optical functionality [16]. Therefore, tuning their band gap and defect chemistry through controlled doping is essential for designing next-generation multifunctional composite materials.

SYNTHESIS

Both undoped and cobalt-doped titanium dioxide (TiO₂) together with zinc oxide (ZnO) nanoparticles were prepared using analytical-grade reagents that were not subjected to extra purification. Titanium tetrachloride, ethanol, cobalt chloride hexahydrate, zinc acetate dihydrate, and an ammonia solution with 28–30% concentration were required for the experiment. Deionised water was important for cleaning, as well as for preparing all the liquids.

Synthesis of TiO₂ Nanoparticles

Preparation of Undoped TiO₂

Undoped TiO₂ nanoparticles were synthesized using the sol-gel method. A mixture of 20 mL TiCl₄ in 80 mL ethanol was stirred at 60°C to form a gel. The pH was adjusted to 1 for gelation, followed by drying at 100°C for 6 hours and calcination at 600°C for 4 hours to produce a white TiO₂ nanopowder (TC0).

Preparation of Co-Doped TiO₂

For cobalt doping, CoCl₂·6H₂O was added to the TiO₂ precursor solution at concentrations of 1%, 3%, and 5% (w/w). The resulting solution was stirred, and the pH was maintained at 3. After drying at 100°C for 6 hours, the samples were calcined at 600°C for 4 hours. The doped samples were designated as TC1, TC3, and TC5.

Synthesis of ZnO Nanoparticles

Preparation of Undoped ZnO

ZnO nanoparticles were synthesized using a co-precipitation method by mixing an aqueous solution of zinc acetate with ammonia to adjust the pH to 8–9. The precipitate was filtered, rinsed, and dried at 80°C for 12 hours, followed by calcination at 400°C for 3 hours to obtain undoped ZnO nanopowder (ZC0).

Preparation of Co-Doped ZnO

For cobalt doping, CoCl₂·6H₂O was added to the Zn acetate solution at concentrations of 3%, 5%, and 7% (w/w) prior to ammonia addition. The synthesis procedure followed the same steps as for undoped ZnO, and the doped samples were designated as ZC3, ZC5, and ZC7.

Characterization Techniques

Various techniques were employed to analyze the structural, morphological, and optical properties of the synthesized nanoparticles:

- **X-ray Diffraction (XRD):** Confirmed crystal structure and phase purity. Crystallite size and strain were calculated using Scherrer and Williamson-Hall analyses.
- **Scanning Electron Microscopy (SEM):** Visualized the surface morphology and particle distribution.
- **Energy Dispersive X-ray Spectroscopy (EDX):** Validated elemental composition and doping levels.
- **Transmission Electron Microscopy (TEM):** Provided high-resolution images for particle size and crystallinity assessment.
- **Fourier Transform Infrared Spectroscopy (FTIR):** Identified functional groups and the formation of metal-oxygen bonds.
- **UV-Visible Spectroscopy:** Analyzed optical absorption and determined bandgap energies through Tauc plots.
- **Photoluminescence (PL) Spectroscopy:** Explored defect states and recombination mechanisms. PL spectra were recorded using both a commercial fluorimeter and a lab-made setup with laser sources at 405 nm, 488 nm, and 532 nm.

RESULTS AND DISCUSSION

X-ray Diffraction (XRD) Analysis of TiO₂ and ZnO Nanoparticles

XRD analysis confirmed that cobalt doping in TiO₂ and ZnO resulted in minor changes to the crystalline structure without altering the anatase phase of TiO₂ or the wurtzite phase of ZnO. The crystallite sizes of TiO₂ and ZnO nanoparticles were calculated using the Scherrer equation, with values ranging from 10 to 12 nm for TiO₂ and from 27 to 38 nm for ZnO, depending on the doping concentration. The Williamson-Hall analysis revealed compressive strain in both TiO₂ and ZnO samples, with doping leading to slight modifications in lattice parameters.

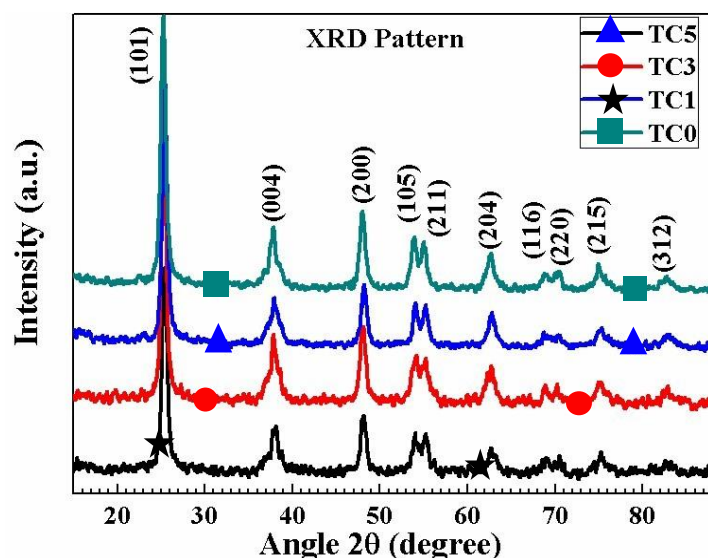


Figure 1. X-ray diffraction patterns of undoped TiO₂ and Co-doped TiO₂ nanoparticles, showing the anatase phase and the effects of Co doping on crystallite size and lattice strain.

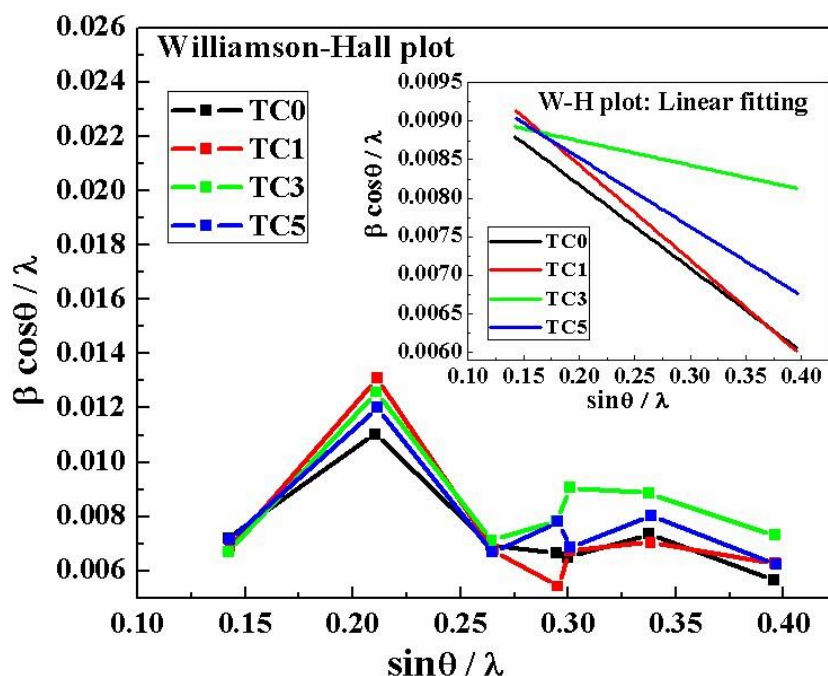


Figure 2. Williamson-Hall plot for undoped TiO₂ and Co-doped TiO₂ nanoparticles, illustrating the presence of compressive strain in all samples.

The peaks observed in the XRD patterns were analysed through a Gaussian function to determine the peak positions (2θ values) and the full-width at half-maximum (FWHM). By employing these values, the lattice parameters, crystallite dimensions, lattice deformations (through Williamson-Hall plots), and crystal densities were determined. The Williamson-Hall analysis indicated the presence of compressive strains across all samples, which were linked to diminished lattice volumes following the doping process. The sizes of the crystallites were calculated employing the Scherrer equation, revealing values within the spectrum of 10 to 12 nm. The dimensions of the unit cell (a , b , and c) for tetragonal TiO₂ were ascertained through the application of Bragg's law and validated by lattice constant equations. Significantly, the incorporation of cobalt resulted in minor modifications to the lattice constants while

preserving the anatase phase, without the emergence of any secondary phases identifiable through XRD analysis. The XRD patterns for ZnO and Co-doped ZnO samples (Figure 3) revealed distinct sharp peaks at 2θ angles of 31.7° , 34.4° , and 36.2° , which are associated with the (100), (002), and (101) crystallographic planes. The sizes of the crystallites were determined employing the Scherrer equation, revealing a growth from 27 nm (ZC0) to 38 nm (ZC7). The lattice constants for the hexagonal wurtzite structure (where $a = b \neq c$) were determined, and no additional Co-related phases were observed, indicating the effective substitution of Co^{2+} ions into the Zn^{2+} lattice positions.

The following Table 1 encapsulates the structural characteristics of TiO_2 and ZnO nanoparticles, detailing aspects such as crystallite dimensions, lattice parameters, strain levels, and dislocation density.

Table 1. Structural parameters of Co-doped TiO_2 and ZnO nanoparticles, including crystallite size, lattice constants, strain, and dislocation density.

Property	TiO_2 (Undoped)	TiO_2 (1% Co)	TiO_2 (3% Co)	TiO_2 (5% Co)	ZnO (Undoped)	ZnO (3% Co)	ZnO (5% Co)	ZnO (7% Co)
Crystallite Size (nm)	10.9	11.3	11.5	10.8	27	41	37	38
Lattice Constants ($\text{\AA}$)	$a = b = 3.788$, $c = 9.504$	$a = b = 3.759$, $c = 9.471$	$a = b = 3.781$, $c = 9.480$	$a = b = 3.765$, $c = 9.462$	$a = b = 3.253$, $c = 5.2102$	$a = b = 3.254$, $c = 5.2113$	$a = b = 3.247$, $c = 5.2012$	$a = b = 3.248$, $c = 5.2026$
Strain (10^{-3})	-0.0108	-0.0123	-0.0031	-0.0089	1.40	1.00	1.04	1.02
Dislocation Density ($\times 10^{15} \text{ m}^{-2}$)	1.37	0.59	0.73	0.69	1.37	0.59	0.73	0.69
Band Gap (eV)	2.8	2.8	2.4	2.5	3.14	2.84	2.82	2.77

The Williamson-Hall plots (Figure 1 for TiO_2 and the corresponding figure 2 for ZnO) provide additional insight into the variations in strain observed across the samples. A downward slope in the Williamson-Hall (W-H) plot for TiO_2 signifies compressive strain, whereas ZnO samples exhibited a diminishing strain trend as Co doping increased. Fluctuations in band gap, illustrated through UV-visible spectral graphs, are linked to doping levels, indicating promising uses in optoelectronic devices and photocatalytic processes.

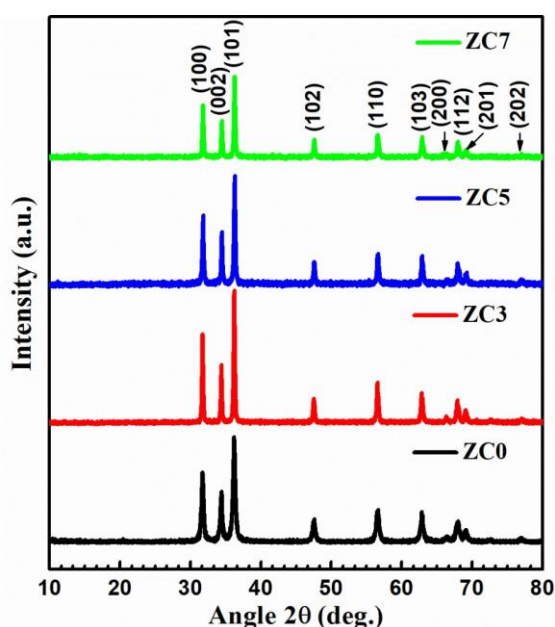


Figure 3. X-ray diffraction pattern of undoped ZnO (ZC0), 3% at (ZC3), 5% at (ZC5) and 7% at (ZC7) Co-doped ZnO samples.

These structural improvements indicate that the Co-doped TiO₂ and ZnO nanoparticles can be incorporated into polymer composites to enhance the mechanical strength and light absorption properties of the materials, especially for applications requiring enhanced photocatalytic or optical functionality.

Surface Morphology of TiO₂ and ZnO Nanoparticles

SEM and TEM images indicated that cobalt doping significantly influenced the morphology of the nanoparticles. For TiO₂, spherical and granular shapes were observed, with slight aggregation in higher doping levels (5% Co). ZnO exhibited a transition from spherical to rod-like structures at moderate doping (3% Co), with further doping leading to a reversion to spherical nanoparticles. These morphological changes are attributed to the role of Co ions as nucleation centers, guiding crystal growth.

Scanning Electron Microscopy (SEM)

Figures 4 (a) and 4 (c) illustrate the SEM images of the undoped TiO₂ (TC0) and the TiO₂ nanomaterials doped with 5% at Co (TC5), respectively. The uneven distribution of nanoparticles, both spherical and granular in shape, is distinctly observable in the micrographs. The corresponding elemental mapping is shown in Fig. 4(b) and Fig. 4(d).

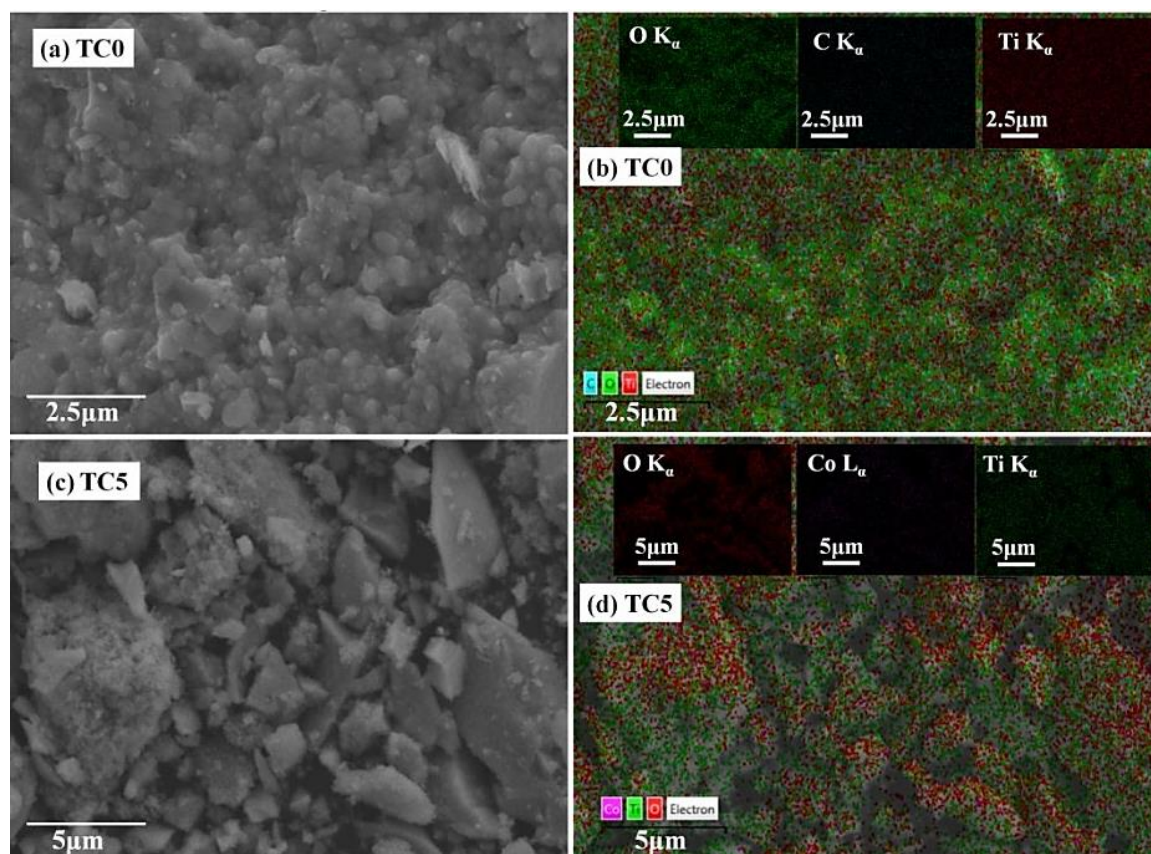


Figure 4. SEM images of undoped and Co doped TiO₂ nanoparticles, Elemental mapping of (a) TC0 (undoped TiO₂), (c) TC5 (5% Co doped TiO₂).

Figure 5 (b) and Figure 5 (d) show the results of the elemental mappings performed on the two samples, correspondingly. With the exception of cobalt, the mapping shows that the atomic ratios of all the other compositional components are evenly dispersed over the sample. Figures 5(a) and 5(c) show the EDX spectra for undoped and Co doped TiO₂ nanoparticles. Three specimens—TC0, TC3, and TC5—are shown in Figure 6 (a-f) using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). By carefully touching and viewing the specimens on

carbon tape, the carbon (C) peak inside the sample may be seen, allowing for accurate microscopic evaluations. Because no further impurity peaks were detected in the samples, it is concluded that the TiO_2 nanoparticles do not have any other crystalline or amorphous phase structures.

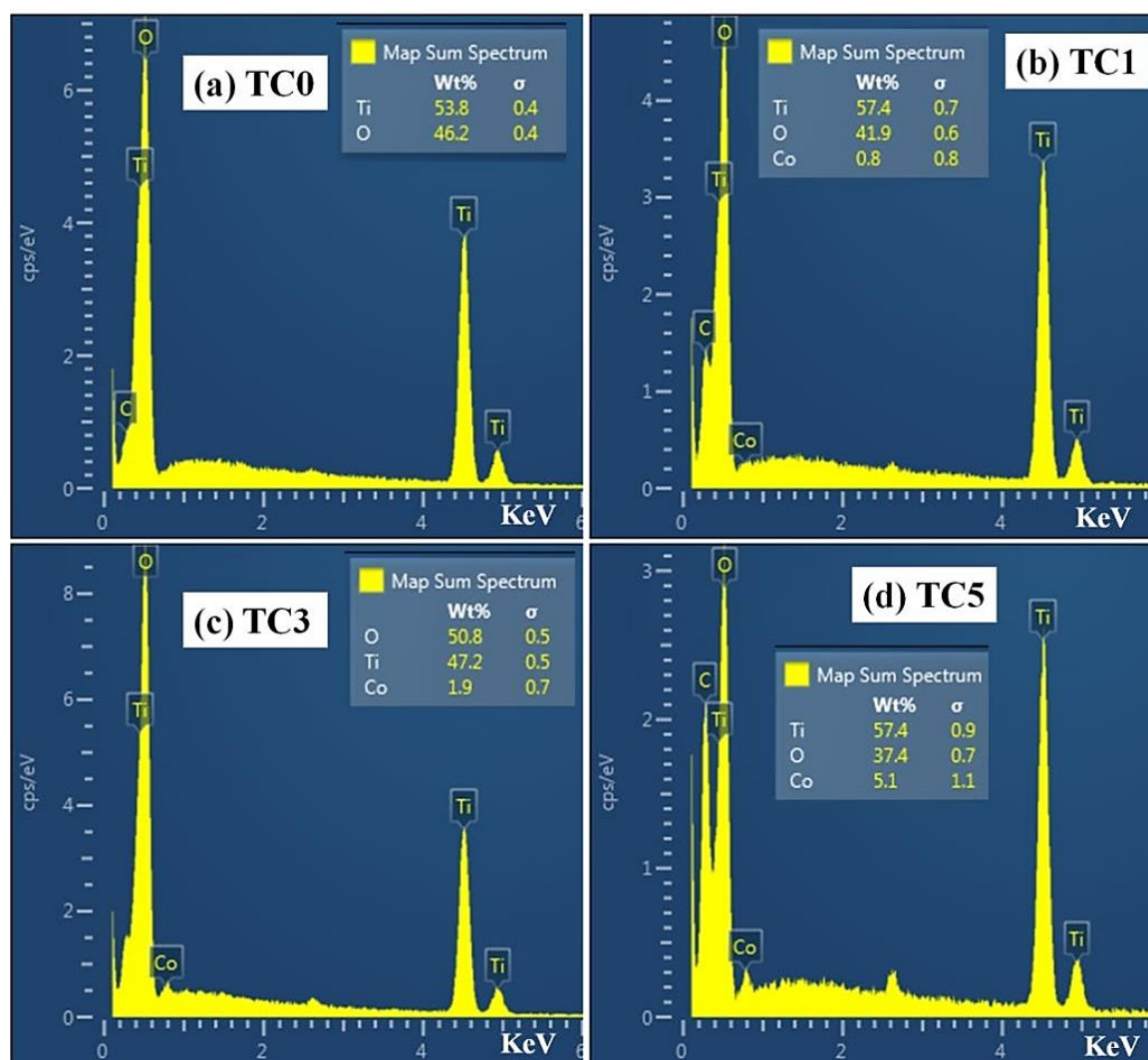


Figure 5. EDX spectra for undoped and Co doped TiO_2 nanoparticles; (a) TC0, (b) TC1, (c) TC3, and (d) TC5.

Transmission Electron Microscopy (TEM)

Three specimens—TC0, TC3, and TC5—are shown in Figure 6 (a-f) using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Additionally, the scanning electron microscopy pictures show that the nanoparticles might have a spherical, granular, or aggregated shape. Red borders have been drawn around the individual nanoparticles to make their size and crystallinity more visible. More than a hundred nanoparticles were used to get the average diameter.

The morphological transformation induced by Co doping can be beneficial for their dispersion and integration into polymer matrices, potentially improving the stability and distribution of the nanofillers in composite systems, thereby enhancing their overall performance.

Surface Morphology ZnO

By using FE-SEM and TEM methods, the surface properties of ZnO samples that were either undoped or doped with Co were examined. Figures 8, 9, and 10 show the SEM and TEM pictures,

correspondingly. One interesting finding from the scanning electron microscopy study is that the ZC3 sample has a structure that looks like rods. Images captured by transmission electron microscopy (TEM) at different magnification levels and taken from different parts of the samples (Fig. 8 and Fig. 9) provide further evidence of similar morphologies. The presence of cobalt ions is associated with the change in shape. Images captured by scanning electron microscopy and transmission electron microscopy show that the uncoated ZnO nanoparticles' surface nanoclusters have granular or nearly spherical forms, or they cluster together with smaller nanoparticles.

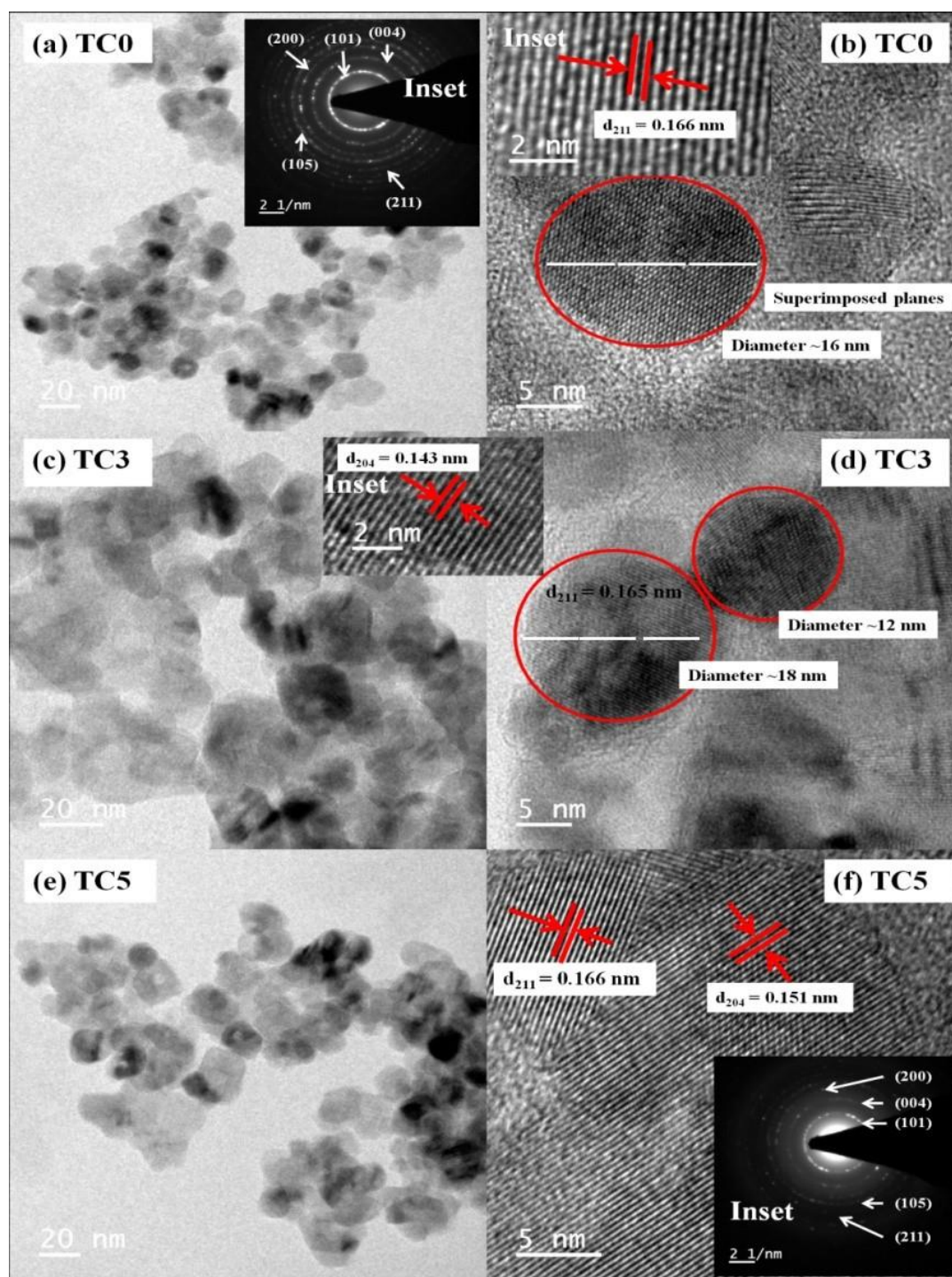


Figure 6. TEM images (a) TC0 (In inset SAED pattern), (c) TC3, (e) TC5; and HRTEM images (b) TC0 (inset at 2 nm scale), (d) TC3 (inset at 2 nm scale), (f) TC5 (In inset SAED pattern).

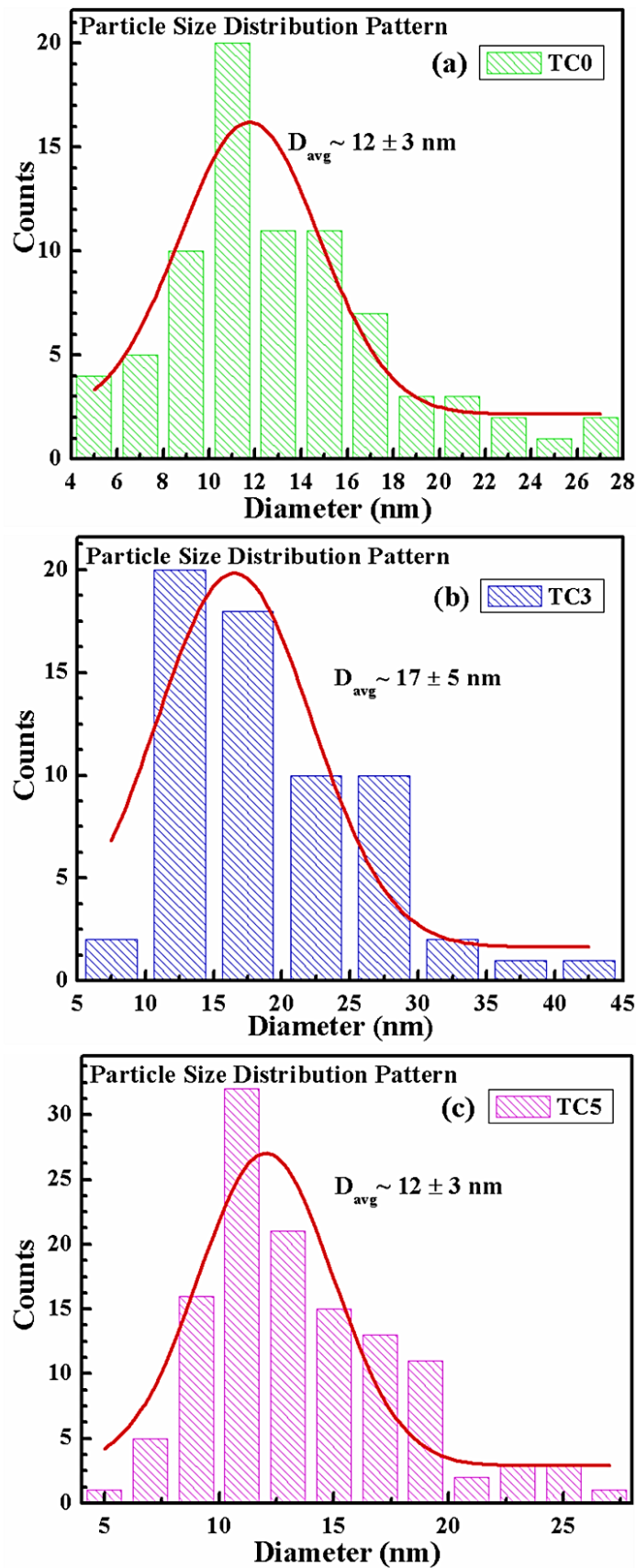


Figure 7. Histograms for particle size distribution curve and their Gaussian fitting (a) TC0, (b) TC3, and (c) TC5

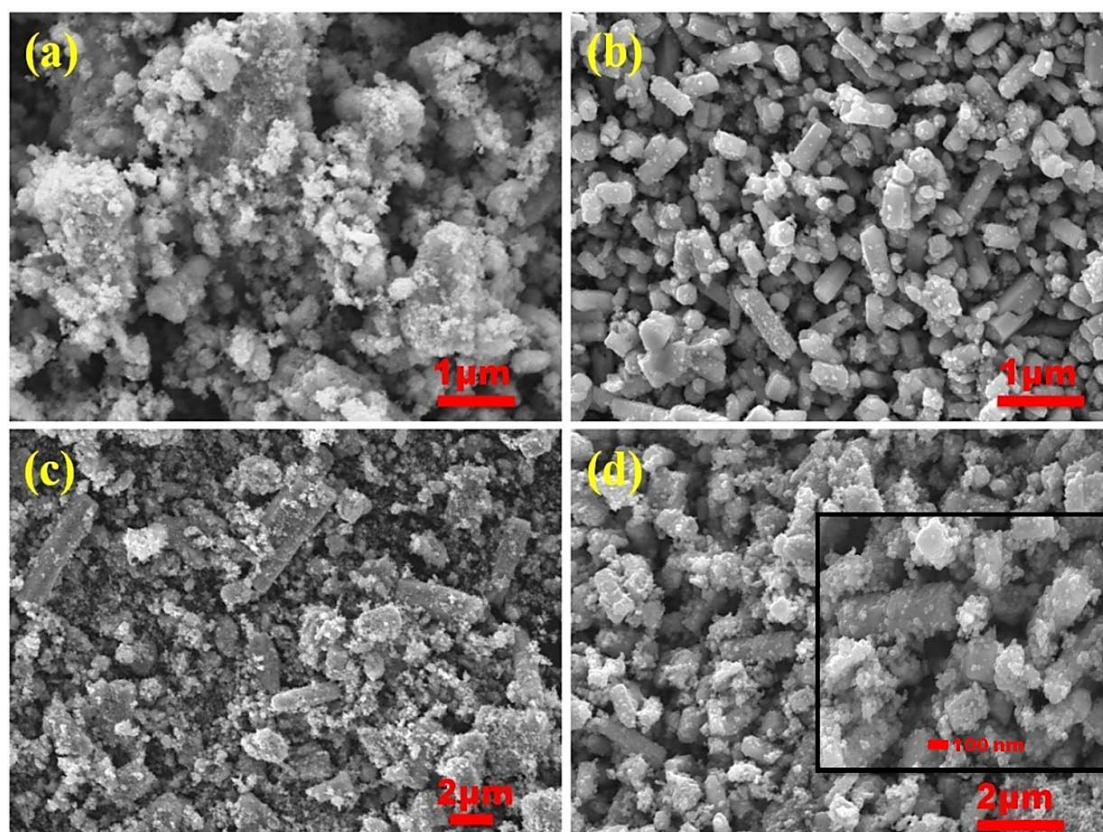


Figure 8. SEM images of (a) ZC0, (b) ZC3, (c) ZC5 and (d) ZC7 samples.

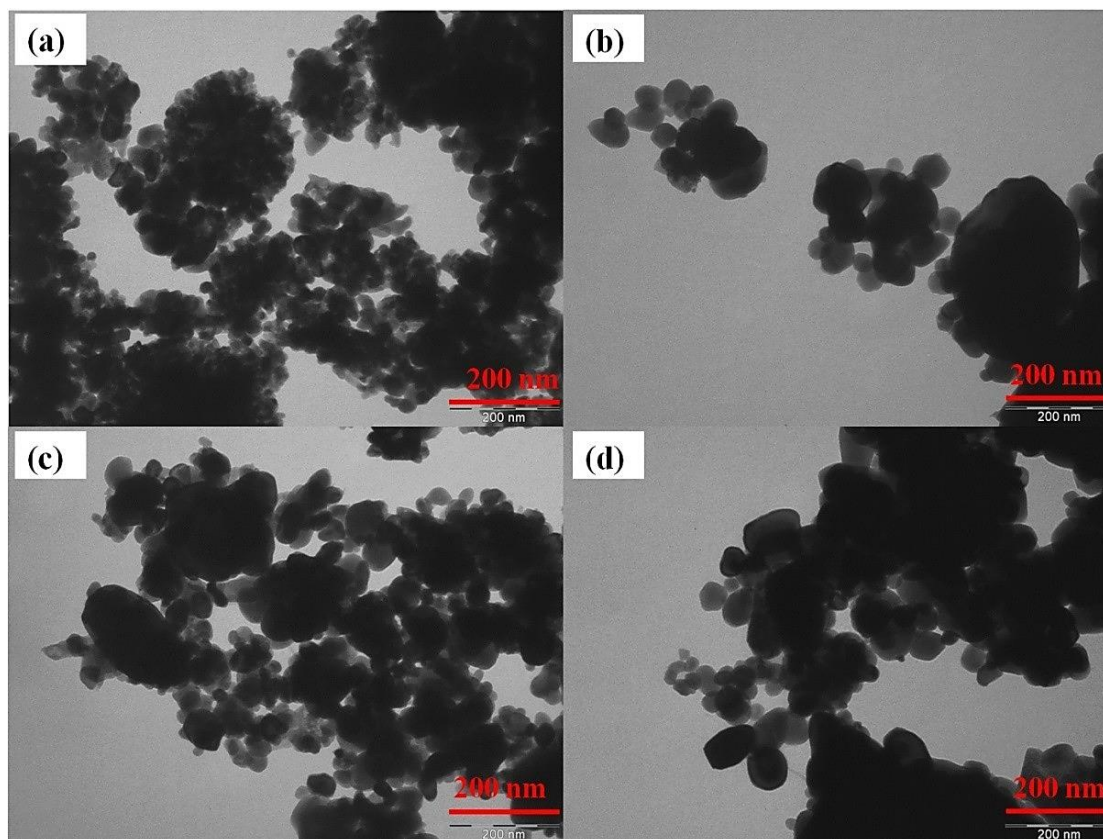


Figure 9. TEM images of (a) ZC0, (b) ZC3, (c) ZC5 and (d) ZC7 samples.

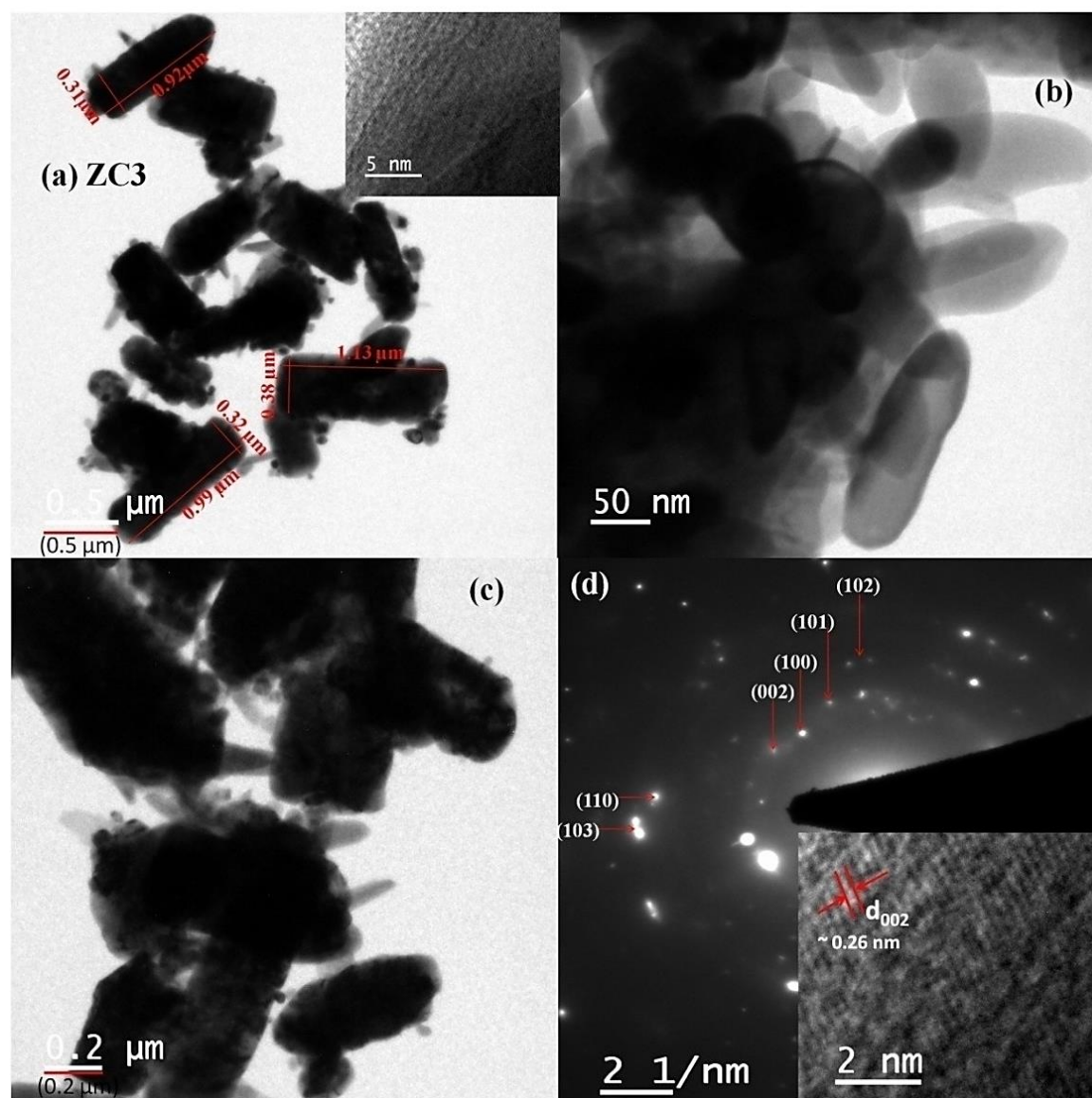


Figure 10. TEM images of ZC3 sample focused in different regions of the sample: (a) at 0.5 μm scale bar, (b) at 50 nm scale bar, (c) at 0.2 μm scale bar, and (d) SAED pattern of ZC3 sample. The insets in (a) and (d) are HRTEM images of ZC3 sample at 5 and 2 nm scale bar respectively.

After adding 3% at Co doping, it's clear that most of the spherical nanoparticles have turned into rod-like nanostructures of varying sizes, with the smaller spherical nanoparticles dispersed around these rod-like forms. The concentration of the rod-shaped nanoparticles decreases with further doping of Co ions up to 7% at, whereas the concentration of the spherically shaped nanoparticles significantly increases. The presence of tiny spherical nanoparticles attached to bigger rod-shaped nanoparticles is plainly seen in all transmission electron micrographs. There is prior documentation of a similar shape for Ag-doped TiO_2 nanoparticles during their polymorphic transition from the anatase phase to the rutile phase [37].

Recent findings by Han *et al.* [21] reveal that ZnO nanostructures undergo notable morphological transformations in response to varying levels of Co doping. This transition involves a progression from spherical nanoparticles to irregular shapes, ultimately forming triangular structures. The adsorption of Co ions on specific facets or the surface of the host material during chemical reactions and thermal annealing appears to be a key factor driving these morphological changes. These processes facilitate

the evolution of ZnO nanostructures from spherical to rod-like morphologies, with the rod-like forms acting as intermediates that bridge the irregular nanoparticles, aiding nucleation [21]. Beyond influencing lattice substitution, Co ions significantly impact the surface properties of the host nanocrystals, leading to altered morphologies. High-resolution transmission electron microscopy (HRTEM) images of the ZC3 sample (shown in Fig. 10) and the selected area electron diffraction (SAED) pattern in Fig. 10(a)-(d) further corroborate these observations. The images and diffraction pattern highlight multiple diffraction planes, underscoring the polycrystalline nature of the samples.

The alterations in bond structure and defect levels can enhance the interaction between the nanoparticles and polymer matrices, leading to better bonding and improved mechanical and photocatalytic properties of polymer nanocomposites.

Fourier Transform Infrared Spectroscopy (FTIR) of TiO₂ and ZnO Nanoparticles

Fourier Transform Infrared Spectroscopy (FTIR) TiO₂

To identify the presence of different bonds and their associated vibrational modes, Fourier-transform infrared (FTIR) spectroscopy was performed on both undoped and cobalt-doped TiO₂ nanoparticles synthesized at 600 °C. The resulting spectra, presented in Figure 11, reveal critical information about the chemical structure of the samples. In the transmittance spectrum, the broad region between 3400 and 3600 cm⁻¹ corresponds to the free stretching vibrations of O-H groups attached to the surface of TiO₂. Additionally, a distinct peak observed near 1630 cm⁻¹ is attributed to the bending vibrational mode of water molecules adsorbed on the nanoparticle surfaces [8]. These findings underscore the influence of surface-bound species on the vibrational characteristics of the materials, offering deeper insights into their structural and chemical properties.

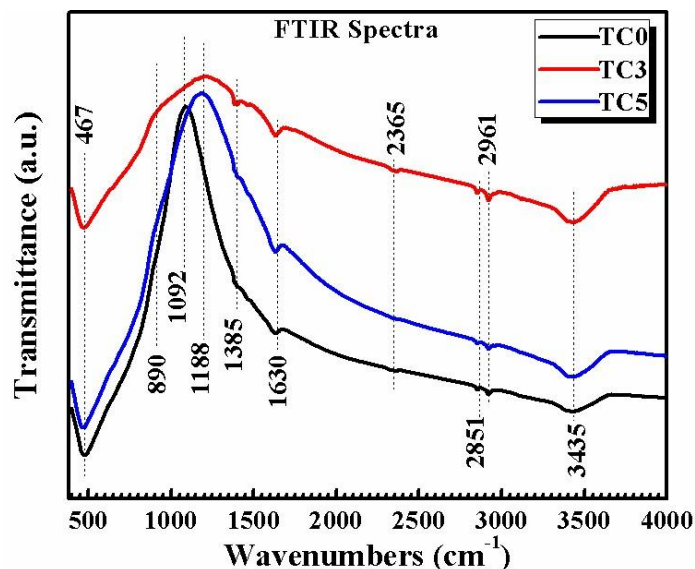


Figure 11. FTIR spectra undoped TiO₂ and Co doped TiO₂ nanoparticles.

The anatase phase of titanium dioxide is characterized by prominent FTIR absorption bands appearing below 1200 cm⁻¹, which are primarily associated with Ti-O and Ti-O-O bond vibrations [8,9,14]. Below Table 2 outlines the specific peak positions along with their likely vibrational modes. These peaks are typically indicative of the lattice dynamics and bond interactions within the TiO₂ framework. Key vibrational modes include those in the range of 500–800 cm⁻¹, often linked to the symmetric and asymmetric stretching of Ti-O-Ti bonds, while lower-frequency signals, generally below 500 cm⁻¹, correspond to Ti-O bending vibrations. The detailed peak assignments provide essential insights into the structural characteristics of the anatase phase, offering confirmation of its formation. This analysis also highlights the role of bonding and lattice vibrations in defining the material's phase-specific properties, which are vital for its functional applications.

Table 2. FTIR Peak's position

FTIR Peak position/group name	TC0 cm ⁻¹	TC3 cm ⁻¹	TC5 cm ⁻¹
Absorption Ti=O/Co=O	478	475	467
Absorption Ti=O	890	891	889
Ti-O-Ti/Co=O	1092	1150	1144
Ti-O-Ti	-	1217	1188
CO ₂	1385, 1400	1385,1402	1385,1402
COO symmetric	1467	1468	1466
(-OH) water/moisture	1630	1630	1630
(O=C=O stretching of Co ₂) CO absorption on -Ti ⁴⁺	2350	2338,2363	2365
C-H stretching (saturated hydrocarbons)	2851, 2920	2851, 2922	2852, 2922
C-H stretching (saturated hydrocarbons)	2961	2960	2970
free stretching O-H vibration of water/moisture	3435	3437	3433
(Ti-OH)	3653	3653	3653

Building on the detailed spectral analysis, the observed absorption peaks provide a comprehensive understanding of the structural and chemical interactions within the doped and undoped TiO₂ nanoparticles. The absorption features near 478, 475, and 467 cm⁻¹ are primarily attributed to M=O bonding, where M refers to Ti in undoped samples (TC0) and to a combination of Ti and Co in doped samples (TC1, TC3, and TC5). This concurrent presence highlights the influence of doping on the lattice vibrations and chemical bonding [11,13,18]. As discussed by Choudhury *et al.*, the shift in peak positions below 500 cm⁻¹ towards lower wavenumbers is a direct result of the formation of Co-O bonds, driven by oxygen vacancies generated during the substitution of Ti⁴⁺ with Co²⁺ ions [11]. Supporting this, findings by S. Kundu and collaborators report Co-O bond vibrational modes appearing at approximately 493 and 660 cm⁻¹ [19]. Meanwhile, the broad bands detected at 1092, 1188, and 1217 cm⁻¹ are assigned to Ti-O-Ti vibrational modes, confirming their role in defining the structural framework of the nanoparticles [8].

Doping with Co also induces a mass reduction in the lattice, which correlates with the observed shifts in peak positions for Co-doped TiO₂ nanoparticles. Peaks in the range of 1385–1402 cm⁻¹ are linked to CO₂ or CO₃ anions, likely formed due to atmospheric adsorption during synthesis and annealing [13]. Additionally, the symmetric stretching vibrations of C-H bonds, detected between 2851 and 2961 cm⁻¹, originate from residual alcohol groups in the nanoparticles, a common byproduct of precursor decomposition [18–20]. Minor peaks observed at 1466, 1468, and 2365 cm⁻¹ are attributed to functional groups involving carbon, hydrogen, and oxygen, excluding TiO₂ itself. These features may arise from ambient contamination or the remnants of saturated hydrocarbons left over from organic precursors used during synthesis and annealing [18–20]. Together, these observations provide a detailed picture of the chemical and structural characteristics of both doped and undoped TiO₂ nanoparticles, emphasizing the role of Co doping in altering their vibrational and bonding properties.

Fourier Transformed Infrared Spectroscopy ZnO

To analyze the presence of various functional groups within the samples, Fourier Transform Infrared (FTIR) spectroscopy was employed. This method provides valuable insights into the molecular structure, crystalline framework, and any inter- or intramolecular interactions present in the materials. During the FTIR measurements, KBr pellets were utilized as a reference medium. The resulting spectra, spanning the wavenumber range of 4000 to 400 cm⁻¹, are illustrated in Figure 12 for both uncoated ZnO and Co-doped ZnO nanoparticles, specifically samples ZC3, ZC5, and ZC7. In the undoped ZnO sample, absorption bands were identified at 3439, 2924, 2852, 2371, 2346, 1745, 1578, 1454, and 502 cm⁻¹. A distinct peak observed near 502 cm⁻¹ corresponds to the stretching vibrations of Zn-O bonds in a tetrahedral configuration, serving as confirmation of ZnO nanoparticle formation [26]. In Co-doped ZnO samples, this peak shows a subtle shift to higher wavenumbers, which can be attributed to the

formation of Co-O bonds and the oxygen vacancies that arise when Zn²⁺ ions are substituted with Co²⁺ ions in the ZnO lattice [1,34,35]. The substitution of Zn²⁺ by Co²⁺ ions in the lattice creates localized oxygen defects, often referred to as singly charged oxygen vacancies ($OOaa^+$), due to the relatively low energy required for their formation [22]. Despite the introduction of cobalt and its associated lattice modifications, no significant displacement of peaks was observed when comparing similar functional groups across different samples. These findings highlight the stability of the ZnO lattice while showcasing the subtle changes induced by Co doping.

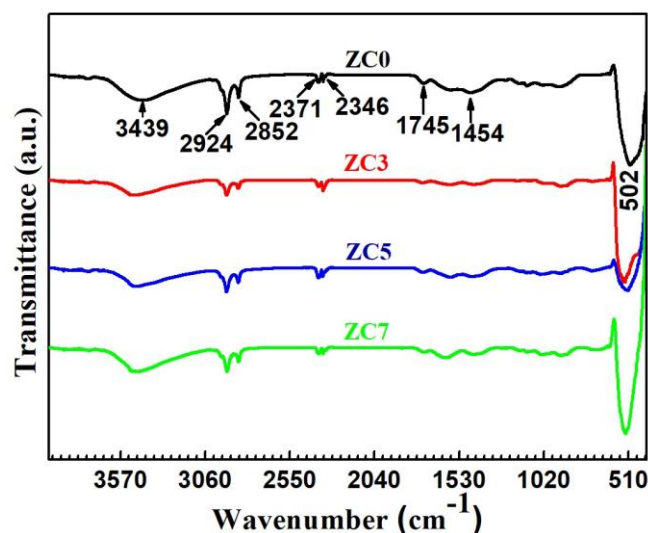


Figure 12. FTIR spectra of undoped ZnO (ZC0) and Co-doped ZnO (ZC3, ZC5 and ZC7) samples.

Additionally, the broad band at 3439 cm⁻¹, attributed to the stretching vibrations of hydroxyl (O-H) groups within H₂O molecules, indicates their integration within the Zn-O and Zn-Co-O lattice structures [6,11,31]. The absorption peaks at 2924 cm⁻¹ and 2852 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of H-C-H groups, respectively, signifying the presence of alkyl residues. Stretching vibrations of gaseous carbon dioxide (O=C=O) molecules are responsible for the absorption maxima at 2371 cm⁻¹ and 2346 cm⁻¹, further confirming atmospheric adsorption during sample preparation or handling [29,36]. Additional absorption peaks identified at 1745, 1578, and 1454 cm⁻¹ are linked to the functional groups comprising carbon, hydrogen, and oxygen, likely originating from saturated hydrocarbons derived from organic remnants in the precursors [17]. The absence of impurity peaks associated with CO (857, 713 cm⁻¹) and CO₃ (598 cm⁻¹) confirms the successful removal of secondary impurity phases during synthesis and annealing processes [17,31]. This thorough spectral analysis underscores the purity of the synthesized samples while highlighting the molecular interactions within the ZnO and Co-doped ZnO lattices. The absence of secondary impurities, alongside the distinct peaks attributed to specific functional groups, demonstrates the effectiveness of the synthesis protocols employed and the structural integrity of the resulting nanoparticles.

UV-visible (UV) Spectra of TiO₂ and ZnO Nanoparticles

UV-visible (UV) Spectra TiO₂

The shift from O 2p levels in the VB to Ti 3d energy states in the CB has been better understood by studying the UV-Vis absorption characteristics of these nanoparticles. The UV-Vis absorption spectra of the samples are shown in Figure 13. The Tauc plot that was used to determine the indirect bandgap of these samples is shown in Figure 14 (a and b). The absorption band gap energy may be calculated using the following formula [9].

$$(\alpha h\nu)^n = B (h\nu - E_g) \quad (\text{Eq. 1})$$

In this particular situation, the variables $h\nu$, α , B , and n vary according to the kind of transition; for example, $n = 2$ for a direct band gap, $2/3$ for a direct prohibited gap, and $1/2$ for an indirect band gap.

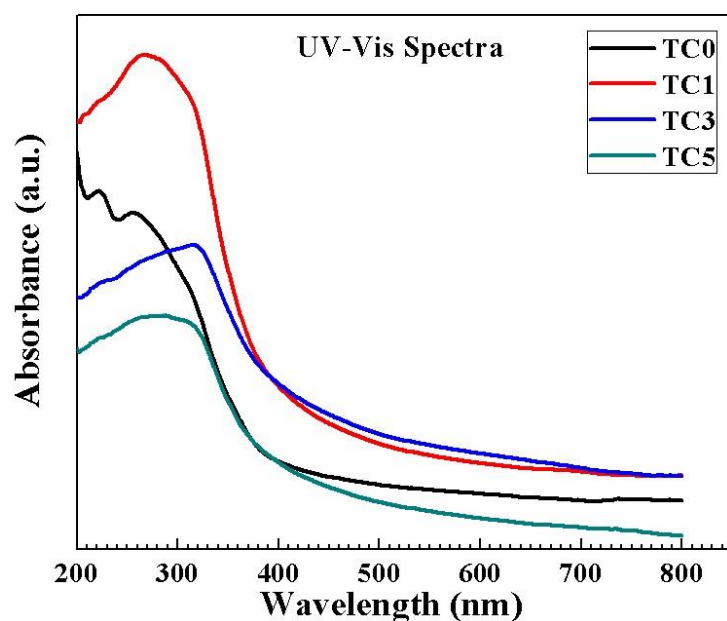


Figure 13. UV-Vis spectra of undoped TiO₂ and Co doped TiO₂ NPs.

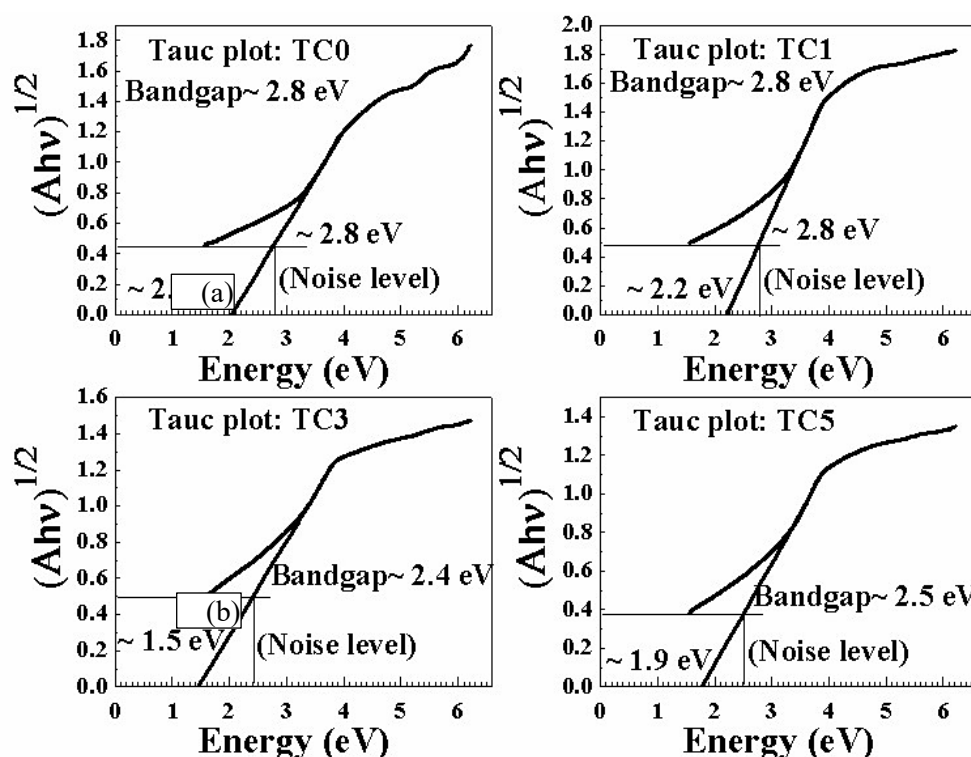


Figure 14. Tauc plot for undoped and Co doped TiO₂ nanoparticles. (a) Noise may arise because of background correction, and (b) unavoidable scattering and errors in instrument response function.

In accordance with Beer's law, the absorption coefficient (α) and absorbance (A) are directly related. The bandgap may be found by modifying and extending the linear region's tail from the inflection point to the $Y=0$ axis of the Tauc plot, which shows $(Ah\nu)^{1/2}$ as a function of $h\nu$ (photon energy). Use of direct extrapolation from Tauc plots, without taking noise levels into account, yields indirect bandgap values of 2.1 eV for undoped TiO₂ (TC0), 2.2 eV for 1% at (TC1), 1.5 eV for 3% at (TC3), and 1.9 eV for 5% at (TC5) Co-doped TiO₂ nanoparticles, respectively. As pointed out by Pallotti *et al.* [21], the results are unsupported, hence removing the background is crucial. After removing the noise from the

Tauc plots, the resultant indirect bandgap values for TC0 and TC1 are 2.8 eV, TC3 is 2.4 eV, and TC5 is 2.5 eV, as previously stated.

UV-visible (UV) Spectra ZnO

The UV-Visible absorption and reflectance spectra for both pure ZnO and Co-doped ZnO are presented in Fig. 14 (a) and Fig. 14 (b), correspondingly. The assessment of the direct band gap energy was conducted utilising the equation [4,37]:

$$(\alpha h\nu)^2 = A (h\nu - E_g) \quad (\text{Eq. 2})$$

In this model, A is a constant, α is the absorption coefficient, h is Planck's constant, ν is the light frequency, and E_g is the material's optical band gap energy. According to Tauc's plot, which shows the relationship between $h\nu$ and $(\alpha h\nu)^2$, as shown in Figure 15 (a-d), the presence of direct electronic transitions in this system has been validated [38]. By extending the linear part of the graph to the point where $(\alpha h\nu)^2$ equals zero, the energy of the optical band gap (E_g) has been determined [18,39]. Pure zinc oxide has a base band gap measured at 3.14 eV. As the concentration of Co in the samples rises, the band gap for the ZC3, ZC5, and ZC7 samples decreases to 2.84 eV, 2.82 eV, and 2.77 eV, respectively.

The decrease in the band gap, commonly known as a red shift, indicates the incorporation of Co⁺² ions into the ZnO lattice [10]. The noted red-shift in the band gap energy is attributed to the sp-d exchange interaction taking place between the band electrons of ZnO and the localised d-electrons of the doped Co⁺² ions. This engagement leads to an enhancement of the O₂p valence band, concurrently diminishing the Zn 4s conduction band (CB) [10,40]. It is believed that the s-d and pd exchange interactions play a role in both negative and positive modifications to the edges of the conduction band (CB) and the valence band (VB), which ultimately leads to a reduction in the band gap [11,18,28]. In addition to the optical band gap transition noted in ZnO and Co-doped ZnO nanoparticles, there are further electronic transitions, as depicted in Fig. 16 (a-b) of the UV-visible reflectance mode spectrum.

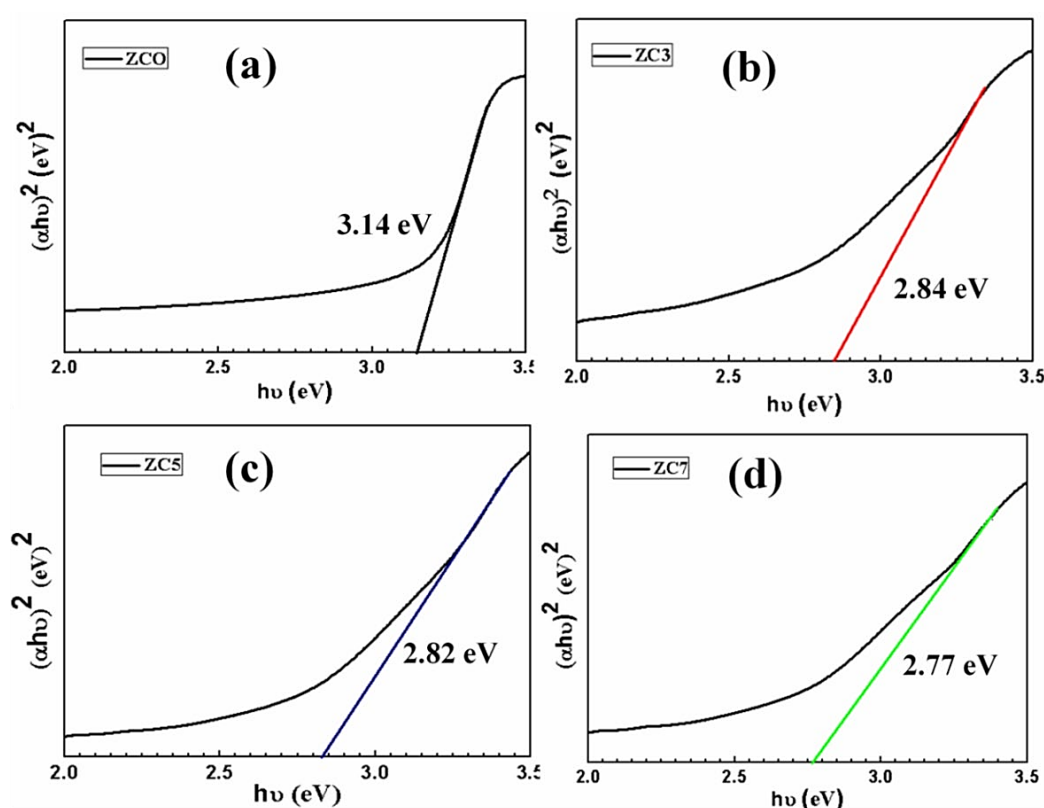


Figure 15. Tauc's plot of (a) ZC0, (b) ZC3, (c) ZC5 and (d) ZC7 samples.

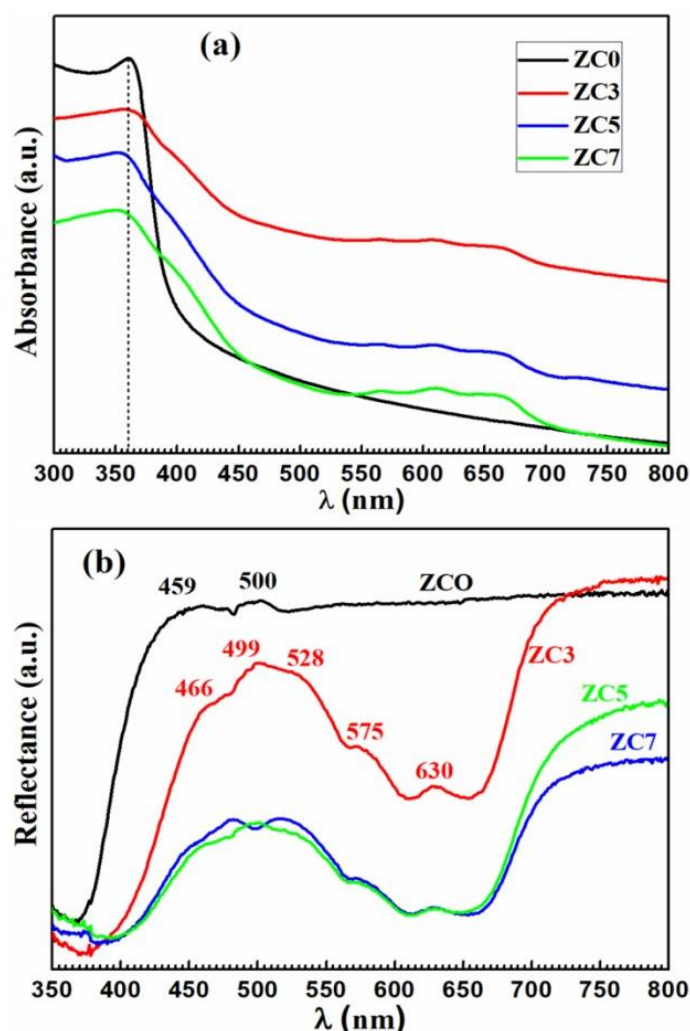


Figure 16. UV-Visible spectra of undoped and Co doped ZnO NP's; (a) absorption mode and (b) reflection mode.

The transitions were noted at 459 and 500 nm for the ZC0 sample, whereas for the ZC3 sample, they were detected at 466, 499, 528, 575, and 630 nm. Similar transitions for the ZC3 sample were observed, although with slightly different peak positions, and this was also the case for the ZC5 and ZC7 samples, respectively. The shifts observed at approximately 459 and 500 nm in the samples can be linked to the direct stimulation of the interstitial Zn (Zni) energy states established within the ZnO lattice [6,18]. Unlike undoped ZnO, the distinct peaks observed at around 528, 575, and 630 nm are exclusively noted to appear after Co doping, particularly in a Co^{2+} ionic state defined by a $3d^7$ high-spin arrangement within a tetrahedral crystal environment [6,18,25]. The transitions associated with $4A_2(F) \rightarrow 2A_1(G)$, $4A_2(F) \rightarrow 4T_1(P)$, and $4A_2(F) \rightarrow 2E(G)$ in high spin states ($S = 3/2$) suggest that the tetrahedrally coordinated Co^{2+} ions proficiently substitute the Zn^{2+} ions in the host lattice [6,18]. The additional transitions noted in Co-doped ZnO samples indicate that these innovative electronic energy levels can be directly stimulated by visible light sources, thus acting as light emitters that display captivating luminescence characteristics. It has been noted that the intensity of these distinctive peaks in the reflection spectra decreases as the concentration of Co rises, suggesting that the additional Co ions are being assimilated into the ZnO occupied sites, which exhibit a diverse local crystal field [6].

The reduced band gap and enhanced visible light absorption make these Co-doped TiO_2 and ZnO nanoparticles ideal candidates for incorporation into hybrid composite materials that require enhanced photocatalytic activity under visible light exposure.

DISCUSSION

Their unique features, such as their amazing stability in chemicals and top-notch function as a semiconductor, have made metal oxide nanomaterials such as titanium dioxide (TiO₂) and zinc oxide (ZnO) adaptable in different fields [30]. Therefore, these properties make them perfect for employment in photocatalysis, optoelectronics, and the cleanup of pollutants [31]. They are very useful, but a trouble with them is that their wide band gaps and low response to light from the sun mean that they can't be widely used. Metal doping is an example of a measure researchers take to improve these characteristics [32]. The presence of cobalt (Co) dopants is a strong way to solve these issues by developing defect states, shrinking the band gap, and altering the crystal structure [33]. The anatase phase of TiO₂, known to be the best for photocatalysis, changes when cobalt is added to its crystal structure [34]. As a result of the change, the band gap drops from 2.8 eV to 2.4 eV and this helps the material to better absorb visible light [35]. Researchers revealed through XRD that cobalt inclusion brings about a stress-compression in TiO₂, which is related to the reduced ionic radius of Co²⁺ in comparison to Ti⁴⁺, by using the Williamson-Hall method [36]. Adapting the structure often improves the way a catalyst works, which matters a lot when it comes to environmental and energy uses [37]. Though both hexagonal wurtzite-structured ZnO and CdO show increase in electrical properties after cobalt doping, ZnO shows different patterns in morphological changes [38]. When the concentration of Co increases in ZnO, the band gap comes down from 3.14 eV to 2.77 eV, strongly contributing to effective use of visible light in photocatalysis [39]. It is the sp-d exchange interactions present between cobalt d-electrons and ZnO band electrons that lead to an increase in the valence band and a decrease in the conduction band, causing the redshift in the absorption, as given by [20]. Through SEM and TEM, scientists found that doping samples with 3% cobalt makes them adopt a shape that looks like a rod, but being doped further with more cobalt again helps them transform into spheres [38]. Cobalt ions in the reaction ensure that growth and the orientation of crystals are guided, according to their function as nucleation centers [37].

Joining the study of Fourier Transform Infrared (FTIR) spectroscopy with Photoluminescence (PL) methods gives better understanding of how adding cobalt to TiO₂ and ZnO alters their structure and optical qualities [38]. The presence of Co-O bonds in FTIR spectra and changes in their vibrations show that the dopant is effectively occupying the MgO lattice [39]. According to photoluminescence research, the peak intensities are lowered in doped samples, which points to less recombination of charge carriers and a necessary improvement in photocatalysis [40]. Cobalt doping of the semiconductor causes defects that stop recombination, so charge carriers live longer and react more effectively [30]. It is further highlighted in these studies that doping greatly increases the optical absorption property of TiO₂ and ZnO, considering the results from UV-visible band gap testing [31]. A smaller band gap in TiO₂ makes it more effective in using solar energy for catalysis. As for ZnO, having a narrower band gap and seeing the edge of its absorption spectrum in higher-energy light helps it more in systems that need the energy from visible light [32]. It was also confirmed that the right amount of doping is what allows for an optimal balance of structural and optical properties in such materials, and this happens with about 3–5% doping [33].

The way the structure, architecture, and optical features change because of cobalt doping shows how carefully the synthesis process should be controlled [34]. These approaches make it possible to evenly add dopants to TiO₂ and ZnO nanomaterials and customise their features [35]. Such approaches allow for the fine changes in dopants, annealing temperature, and proportions of the precursors, all of which influence the material's properties [36]. After this, further studies could develop new ways to improve how these materials perform by combining supplementary elements [37]. Both cobalt-doped TiO₂ and ZnO nanomaterials are promising discoveries in the fields of photocatalysis, optoelectronics, and keeping the environment clean [38]. Precisely altering their features with doping allows them to overcome the boundaries that ordinary materials have, helping them be used in today's advanced technology [39]. Future studies in this area help them become more effective and can bring them to more green energy and environmental solutions [40]. The mixing of cobalt with fuels is best done by focusing on a more even distribution of the cobalt and trying new, more precise ways of mixing it. Most

often, using such doping techniques as sol-gel and co-precipitation helps scientists achieve the desired properties by controlling how much of the dopant is used. When doping levels, annealing temperatures, and precursor mixtures are carefully set, scientists can obtain the needed size, shape, purity, and properties that are significant for the material's performances in photocatalysis and optoelectronics. Mixing cobalt with other elements, for instance nitrogen, carbon, or different transition metals, might help bring additional advancements. The changes made to the structure may make it possible to tighten the band gap, enhance mobility of the charge carriers, and raise the materials' efficiency for catalysis. Besides, teaming up with objects such as graphene or carbon nanotubes can result in outstanding improvements in charge separation and transfer, which, in turn, improve the photocatalytic activity. To show their worth in practice, more analysis must be carried out on how these are affected by long-term exposure and if they are recyclable, given how important these features are for large-scale environmental or energy projects.

TiO₂ and ZnO nanomaterials with cobalt doping are suitable for many new applications, especially in photocatalysis, electronics related to light, and the fight against environmental pollution. Applying specific doping methods, semiconductors can resolve their original issues such as having wide band gaps and low activity for visible light. Since these materials have less of a band gap, more abilities to absorb light, and a low chance of losing electrons, they make great choices for solar energy applications. Still, increasing dopant levels, using different dopants together, and coming up with hybrid materials will play a big role in releasing their full potential. Research will keep being vital for achieving sustainable technology and reducing global problems like energy production and pollution. Making these materials unique for certain uses brings about new prospects for progress in next-generation photocatalytic engineering.

CONCLUSION

This study demonstrates the significant improvements in the structural, optical, and photocatalytic properties of TiO₂ and ZnO nanomaterials through cobalt (Co) doping. Co doping effectively reduces the band gaps of both materials, enhances visible light absorption, and introduces defect states, making them more suitable for applications in photocatalysis and optoelectronics. XRD and TEM analyses confirmed that cobalt ions successfully integrate into the host lattice, maintaining the anatase phase in TiO₂ and the wurtzite phase in ZnO, with no secondary Co-related phases. The incorporation of Co ions results in slight modifications to crystallite size, lattice parameters, and strain, with an observable impact on the surface morphology. SEM and TEM images showed that Co doping induces a morphological transformation in ZnO nanoparticles, shifting from spherical to rod-like structures at moderate doping levels. FTIR and UV-visible spectroscopy further confirmed the changes in the material properties, including the formation of Co-O bonds and a reduction in the optical band gaps. Beyond standalone applications, these Co-doped TiO₂ and ZnO nanoparticles show strong potential as functional nanofillers in polymer nanocomposites, hybrid coatings, and advanced composite materials, where their reduced band gap, enhanced visible light absorption, and engineered defect structure can significantly improve photocatalytic, optical, and environmental performance.

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