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Accelerated Synthesis and Analysis of NiO, ZnO, and ZnO/NiO Materials for Prospective Applications

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This work demonstrates a straightforward, inexpensive, and rapidroute for the synthesis of nickel oxide (NiO), Zinc Oxide (ZnO), and its composite (ZnO/NiO)nanoparticles through the green methodusing Azadirachtaindica (Neem) leaves. The structure, morphology, and elementalconstituents were characterized by X-ray diffraction, scanning electron microscopy,and energy-dispersive X-ray spectroscopy. The energy band gap of pure NiO, ZnO,andZnO/NiO composite was evaluated using the Tauc plot from absorption spectra and resulted as 4.6, 5.1, and 5.2 eV, respectively. The prominent functional groups identified by Fourier-transform infrared (FTIR) spectroscopy. Therefore, comparatively individual NiO and ZnO, semiconductingcomposite-based nanocatalysts such as ZnO/NiO composites arepromising for future industrial applications.
Keywords: Green Synthesis, Azadirachtaindica leaves, Nickel Oxide (NiO), Zinc Oxide (ZnO), ZnO/NiO Nanocomposites.

1. Introduction

NiO-ZnO composites are fascinating materials with many applications, particularly in energy storage and environmental remediation[1]. NiO-ZnO composites are hybrid materials combining nickel oxide (NiO) and Zinc oxide (ZnO) nanostructures. NiO and ZnO are the most studied pseudocapacitive materials, exhibiting reversible redox reactions allowing high-energy storage[1-2]. Combining these two oxides into a nanocomposite can synergistically enhance the electrochemical performance by leveraging the unique properties of each material. These composites exhibit improved properties compared to their components, making them attractive for various applications such as Photocatalysis, Gas sensing, Electrochemical applications, Antibacterial properties, Optical properties, and

Magnetic properties.NiO-ZnOnanocomposites can display interesting magnetic behavior, depending on composition and synthesis method [3-4]. Synthesis methods for NiO-ZnO composites include the sol-gel process, Hydrothermal synthesis, Co-precipitation, Electrospinning, and Chemical vapor deposition. Research on NiO-ZnO composites focuses on optimizing synthesis methods, understanding structure-property relationships, and exploring new applications in environmental remediation, energy storage, and biomedical technologies[5-6]. The rapid growth of energy consumption and the instability of renewable energy sources have highlighted an urge to develop efficient, high-performance energy storage systems [7].

Herein, ZnO, NiO, and ZnO/NiO materials were synthesized using a simple green method. The varied instrumental techniques are focused on studying the characteristic features. For comparative purposes, pristine NiO and ZnO were also evaluated. Finally, the composites are expected to offer more prominent Potential applications.

2. Experimental

2.1 Materials

Azadirachtaindica (Neem) leaves, Zinc acetate dihydrate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$), Nickel acetate dihydrate ($C_4H_{12}NiO_6$) and Sodium Hydroxide (NaOH). All the chemicals were used as received without any further purification.

2.2 Green synthesis of ZnO/NiOnanocomposite

The NiO/ZnOnanocomposite was synthesized by following a green method described by [8]. The green route is an eco-friendly and cost-effective approach to replacing highly toxic and hazardous chemicals. In brief, Azadirachtaindica (Neem) leaves were collected and washed with tap water and then distilled to remove dust particles. The cleaned leaves were dried in a hot air oven at 35°C for 2 hours. Next, 10 grams of the dried leaves were boiled in 100 mL of distilled water at 70°C for 30 minutes and filtered through Whatman filter paper. The resulting leaf extract was stored at 4°C in a refrigerator for later use in synthesizingZnO, NiO, and ZnO/NiO composites.

For synthesizing the ZnO/NiO composite via a green method, 25 mL of A. indica leaf extract was mixed with 50 mL of distilled water in two separate beakers and stirred with a magnetic stirrer at 60°C for 30 minutes. Then, 0.2 M Zinc acetate dihydrate and 0.2 M Nickel acetate dihydrate were added to the solutions containing the leaf extract and stirred under the same conditions. The Zinc acetate dihydrate solution was gradually added to the Nickel acetate dihydratesolution with continuous stirring. The pH of the solution was adjusted to ~7 using 0.5M NaOH aqueous solution, and the mixture was stirred for an additional 6 hours. The precipitate was centrifuged at 3500 rpm for 10 minutes and washed with distilled water and ethanol to remove impurities. The residue was dried in an oven for 6 hours at 60°C and annealed in a programmable furnace at 500°C for 2 hours. Finally, the ZnO/NiOnanocomposite powder was obtained. A similar procedure was used to synthesize pure ZnO and NiOnanomaterials.

2.3 Characterization Techniques

The surface morphology of the synthesized samples was analyzed by a field emission scanning electron microscope (FE-SEM, Carl Zeiss, Ultra Plus). The sample was attached to the carbon tape for the FE-SEM analysis. X-ray diffraction (XRD) (Bruker D8 advance) identified the crystallinity of the synthesized samples. Fourier recognized the functional groups in the as-prepared samplestransform infrared spectroscopy analysis (FTIR-4200). The optical absorption of samples was recorded by a UV-visible spectrophotometer (Analytical Jena, Specord 210 Plus).

3. Results and discussion

3.1. Characteristics of NiO, ZnO,and ZnO/NiO

3.1.1 Powder X-Ray Diffraction Study

Powder X-ray diffraction is the most helpful technique for phaseidentification and structural parameters of the synthesizedmaterials[9]. The X-ray diffraction patterns of ZnO/NiO and the individual phases ofZnO and NiO are depicted in Figure 1. The XRD pattern of NiO inFigure 1 showed that the synthesized material revealedsharpened peaks, indicating the crystallinity of NiO. Thepeaks positioned appearing at 2θ values of 37.35°, 43.40°,63.11°, 75.51°, and 79.45° and each peak is designated as (111),(200), (220), (311), and (222), respectively.These identifiedpeaks were well indexed to the cubic of the NiOphase (JCPDS cared no. 01-073-1519).Thediffraction peaks of ZnO located at 2θof 31.76°, 34.47°,36.23°,47.60°,56.69°,62.78°, 68.12°, and 69.27 indexed torelative planes (100), (002),(101), (102), (110), (103), (112), and (201) are matched to hexagonal phase(JCPDS No. 01-086-3978). The XRD patterns ofZnO/NiO composite contain peaks at 32.2°, 34.74°, 36.6°, 37.12, 43.25°,47.74°,56.95°, 63.03°, 68.20°,69.55°, and 75.24° indexed to hexagonal phase of ZnO crystal planes (100), (002), (101),(111),(102), (110), (103), (112),(220), (112), (201), and (202). These matched thestandard (JCPDS No. 01-080-6504) and agreed with thehexagonal phase. The significant peaks (111), (200), and (220) of NiO appear in the composite pattern. It confirms the excellent bonding between metal oxides and the maintained hexagonal phase. The average crystallite sizes of NiO, ZnO, and ZnO/NiO materials obtained from the Scherrer equation are represented in Table 1. The average crystallite size of theseprepared materials was calculated by applying the Scherrerequation: $D = (K\lambda)/(\beta\cos\theta)$, where D is the average crystallitesize, $\lambda = 1.54056$ Å is the wavelength of Cu kα, β is the fullwidth at half-maximum (FWHM) intensity, θ is Bragg'sdiffraction angle, and K is a constant taken as to 0.94[10-12]. The calculated value in the table is that the averages of the crystallite size from the four peaks of each material are 11.56 nm, 27.32 nm, and 39.51nm NiO, ZnO, and ZnO/NiO, respectively. The average crystallite size of NiO is less than that ZnO and ZnO/NiO composites, possibly due to the mixed oxide formation in the composites

Sno.	Nanoparticles and its Composite	Average Crystalline Size[nm]
1.	NiO	11.56 nm
2.	ZnO	27.32 nm
3.	ZnO/NiO	39.51 nm

Table 1. Averagage Crystalline Size of NiO, ZnO and ZnO/NiO

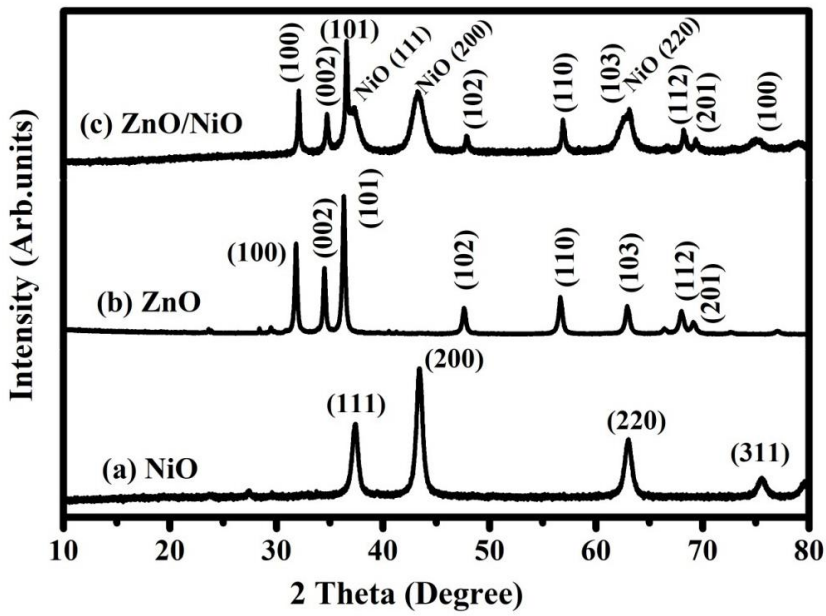

Fig.1. X-ray diffractograms of (a) NiO, (b) ZnO, and (c) ZnO/NiO

3.1.2 Morphology and Elemental Analysis

FESEM images of NiO, ZnO, and NiO/ZnO are shown in Fig:(a–c). Bare ZnO and NiO particles are fine and quasi-spherical. The particles are revealed as relatively agglomerated, whereas the NiO/ZnO composite particles are shown in the dispersed mode. In binary oxide materials, particles appear to be bigger than in individuals. The NiO particles are decked on ZnO in ZnO/NiO. It is plausibly due to the Ni–O–Zn bonding character change. The dispersed surface structure has a higher surface area and positively influences the photocatalytic effectiveness of the material. Energy-dispersive X-ray spectroscopy was investigated to identify the elements present in the prepared materials. Figure 2. (d-f) shows the EDS elemental mappings corresponding to all NiO, ZnO, and NiO/ZnO samples. The presence of elements Ni and O in NiO, Zn, and O in ZnO; Ni, Zn, and O in NiO/ZnO are confirmed without any other impurity species.

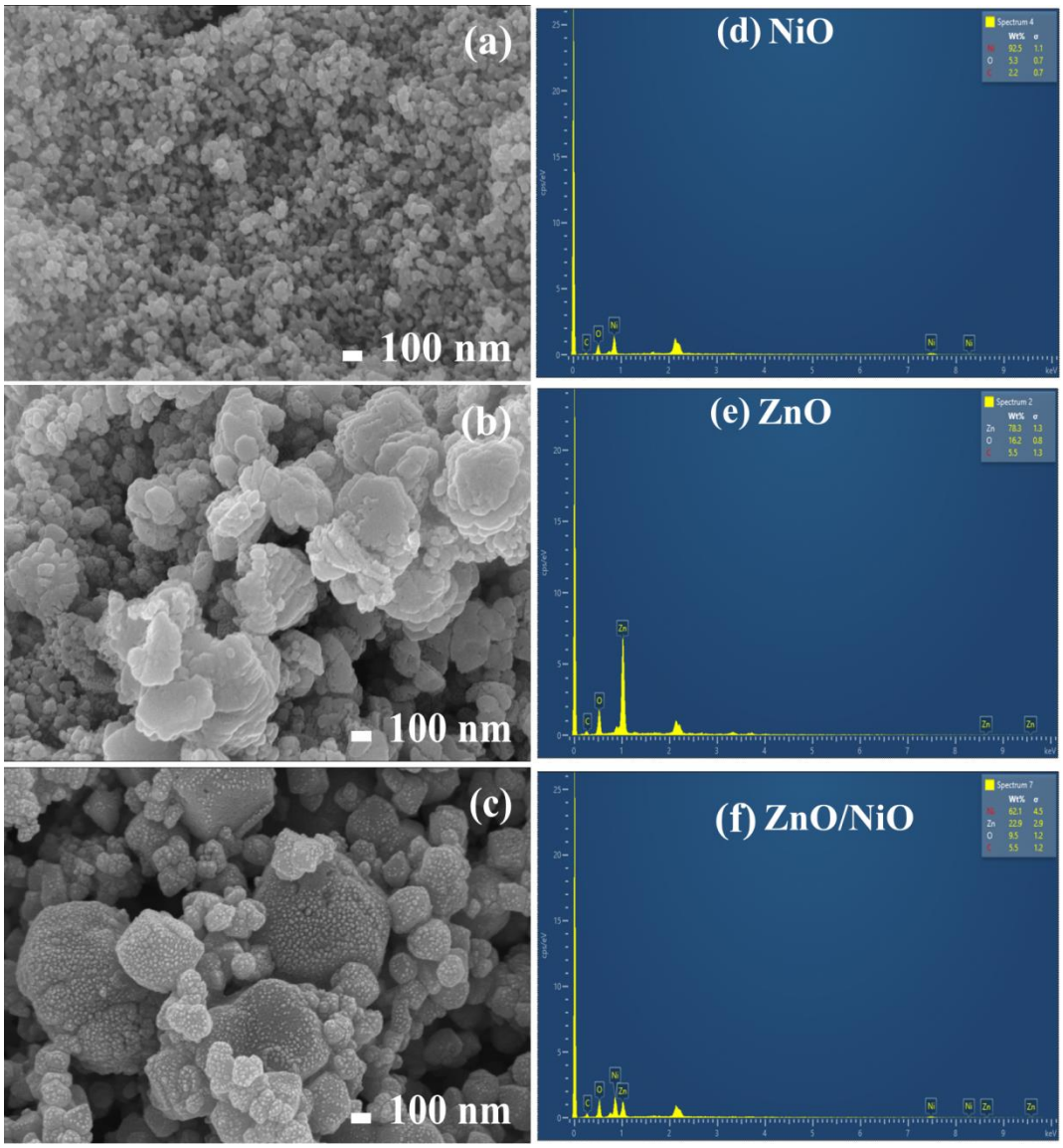

Fig.2. FESEM micrographs of (a) NiO, (b) ZnO, and (c) ZnO/NiO Nanoparticles and their EDS (d-f)

3.1.3 Optical Properties

The optical properties of NiO, ZnO, and ZnO/NiO materials were studied by UV-VIS absorption spectroscopy. The UV–visible absorption spectra of prepared samples NiO, ZnO, and ZnO/NiO are shown in Figure 3(a).

The UV–Vis absorbance of the ZnO/NiO composite obtained was higher than the NiO and ZnO nanoparticles, which implied that ZnO/NiO has relatively better light-harvesting efficiency. The result showed firm absorption peaks at 249, 243, and 236 nm

wavelengths for pure NiO, ZnO,and ZnO/NiO samples. The band gap energy of the prepared samples was evaluated using the Tauc plot and is presented in Figure 3(b). the energy band gaps of NiO, ZnO, and ZnO/NiOcomposites are 4.6, 5.1, and 5.2 eV, respectively.

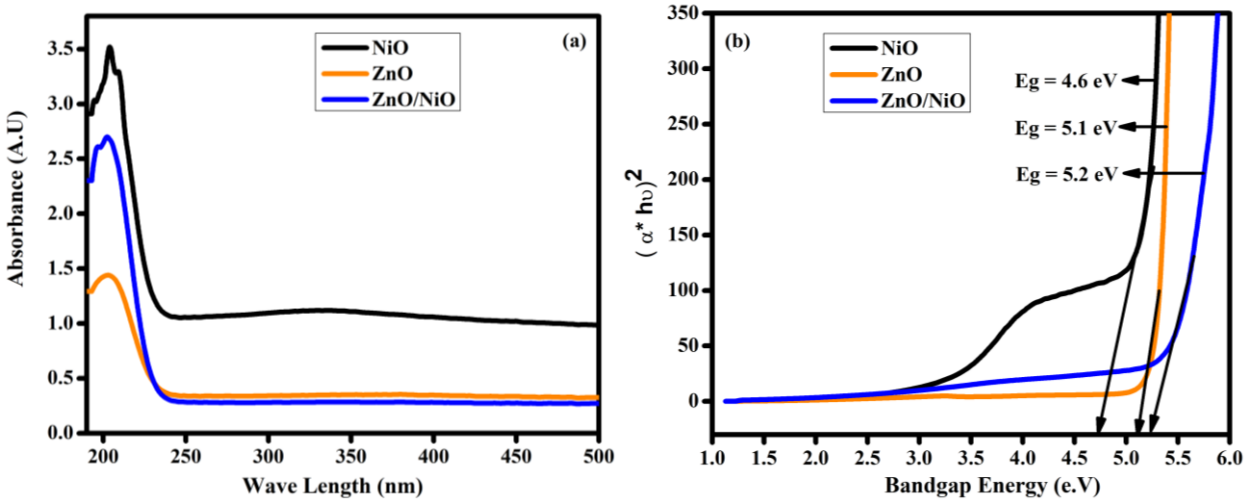

Fig.3. (a) UV- Visble spectra, (b) Tauc Plots of NiO, ZnO, and ZnO/NiO

3.1.4. Vibrational analysis

The Fourier Transform Infrared (FTIR) analysis defines the different functionalgroups in the prepared nanoparticles and nanocomposite.The obtained vibrational peaks are compared with the FTIR library, and functional groups such as carbonate, hydroxyland metal oxide vibrational notes are found[13]. The FTIR spectrum of Nickel Oxide (NiO) exhibits characteristic peaks corresponding to the material's vibrational modes. Peak around 455-465 cm^{-1}: This peak corresponds to the Ni-O stretching vibration. In the NiO crystal structure, the nickel and oxygen atoms are bonded, and this peak arises from the stretching of this Ni-O bond.Peak around 530-550cm^{-1} is attributed to the Ni-O-Ni bending vibration. In the NiO lattice, the oxygen atoms are sandwiched between two nickel atoms, and the bending of this Ni-O-Ni arrangement gives rise to this peak. Peak around 725-735cm^{-1} is associated with the Ni-O-Ni asymmetric stretching vibration. Similar to the previous peak, this mode involves stretching the Ni-O-Ni linkage but in an asymmetric manner. Peak around 840-860cm^{-1} peak can be attributed to the Ni-O-Ni symmetric stretching vibration. In this case, the Ni-O-Ni linkage stretches symmetrically, leading to this higherfrequency peak. Peak around 1400-1420 cm^{-1} is typically assigned to the presence of carbonate (CO_3^{-2}) species on the NiO surface. Carbonate can be introduced due to the adsorption of atmospheric CO_2 on the NiOsurface[14-16].

It's important to note that the exact peak positions may vary slightly depending on factors such as the synthesis method, particle size, and experimental conditions. However, the general assignments mentioned above are widely accepted in the literature for the FTIR characterization of NiO[17-18].The peak around 455-465cm^{-1} corresponds to the Ni-O stretching vibration.The peak around 530-550cm^{-1} is due to the Ni-O-Ni bending

vibration.The peak around 725-735cm^{-1} is assigned to the Ni-O-Ni asymmetric stretching vibration.The peak around 840-860cm^{-1} is associated with the Ni-O-Ni symmetric stretching vibration.The peak around 1400-1420cm^{-1} indicates the presence of carbonate species on the NiO surface.

FTIR spectra of Zinc Oxide (ZnO) typically exhibit distinct peaks that correspond to the characteristic vibrational modes of the material. Understanding these peaks provides valuable insights into the structure and properties of ZnO.The Fundamental absorption peak around 400-500cm^{-1} is corresponds to the fundamental lattice vibration mode of the ZnO crystal structure[19]. It arises from the stretching vibration of the Zn-O bond within the ZnOtetrahedra. The precise position of this peak is influenced by factors such as the crystallinity, defects, and doping of the ZnO material. The shoulder peak of ZnO could be observed in the range of 550-660cm^{-1} which might be due to the polycrystalline or nanostructure of ZnO and also attributed to the bending vibration of the Zn-O-Zn bond within the ZnOtetrahedral.The peaks around 1100-1200 cm^{-1}correspond to the infrared-active optical phonon modes of the ZnO crystal structure[20]. They arise from the transverse optical (TO) and longitudinal optical (LO) phonon modes of the ZnOlattice.The position and splitting of these peaks can be influenced by factors such as doping, strain, and the presence of defects in the ZnO material. The presence of broad peaks in the range of 3300-3600 cm^{-1} indicates the existence of hydroxyl groups on the surface of the ZnOmaterial[21].These OH groups can be adsorbed water molecules or surface hydroxyl groups formed during the synthesis or processing of the ZnO. The intensity and position of these peaks can provide information about the surface chemistry and the degree of hydroxylation of the ZnO[21-23].The analysis of the FTIR spectra of ZnO, including the identification and interpretation of these characteristic peaks, is essential for understanding the material's structural, compositional, and surface properties[24,25]. This information is crucial for various ZnO applications, such as optoelectronics, sensors, catalysis, and energy storage devices.

In ZnO/NiO, the main peaks in the FTIR spectra of ZnO and NiO correspond to the fundamental lattice vibration mode, the bending vibration of the Zn-O-Ni, Zn-O-Zn bond and Ni-O-Ni, the infrared-active optical phonon modes, and the presence of hydroxyl groups on the surface of the material. Due to similar frequencies of Zn-O and Ni-O bond causes to over laping in the composite. The position, intensity, and splitting of these peaks provide valuable insights into the structural, compositional, and surface characteristics of the ZnO/NiO sample.

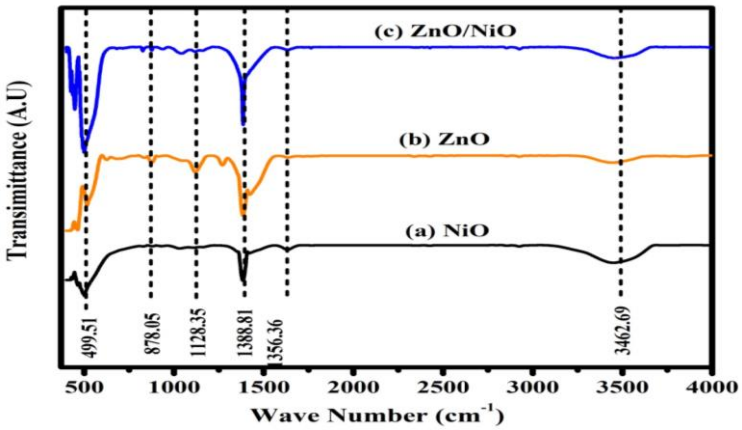

Fig.4. FTIR spectra of (a) NiO, (b) ZnO and (c) ZnO/NiO

4. Conclusions:

A summary of this study presents pure metal oxides (NiO and ZnO), and ZnO/NiO materials have been successfully prepared using the green method. The X-ray diffraction studies emphasized the development of cubic and hexagonal structures of ZnO/NiO composites. The metal oxides synthesized by the process described above possess high purity, as indicated by the XRD patterns. FESEM and EDS studied morphology and elemental investigations,respectively. The compositional analysis was studied using FTIR spectra. Band gap values confirming the obtained materials have a semiconductor band gap range.

Credit author statement

Akumarti Raju: Conceptualization, Methodology, Formal analysis,Investigation, Writing-original draft. Vangapandu Anusha: Data curation,Investigation.Budithi Ravi Kumar: Data curation, Investigation. Gattupalli Manikya Rao: Data curation, Formal analysis, Investigation.

Declaration of competing interest

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

Data Availability Statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can bedirected to the corresponding author.

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