Synthesis and comparative study on the structural and optical properties of ZnO doped with Ni and Ag nanopowders fabricated by sol gel technique

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In this work we have tried to prepare Ni and Ag doped ZnO nanopowders using the sol gel technique. The influence of Ni and Ag (1, 3 and 5 mol.%) on the crystalline structure and optical properties of ZnO was investigated. The samples were characterized by XRD, FTIR and UV–visible spectrophotometer. XRD patterns confirmed the wurtzite formation of doped and undoped ZnO nanopowders. The average crystallite sizes of the prepared samples found from XRD were 19 nm for undoped ZnO, from 17 to 22 nm for Ni-ZnO and from 19 to 26 nm for Ag-ZnO. The average crystallite size of Ag-ZnO increased with increasing Ag contents. Different optical properties of Ni-ZnO and Ag-ZnO nanopowders were observed for different Ni and Ag content. The band gaps of Ni-ZnO and Ag-ZnO nanopowders were lower than that of the undoped ZnO (3.1 eV). The band gaps of Ag-ZnO were lower than that of Ni-ZnO. The optical properties of ZnO were enhanced by Ni (mol.%) in the UV region and by Ag (3 and 5 mol.%) in the visible region.

Nano-sized semiconductors have been attracting more attention due to their size-dependent electrical and optical properties. Nano-sized semiconductor may show different behaviors from the bulk semiconductor. Nano-sized metal oxide such as ZnO, CdO, SiO₂, and PbO with different nanocomposites for example PbO–CdO¹, CdO–SiO₂² and CdO–ZnO³ have been prepared by using different methods such as sol–gel and co-precipitation techniques. Nanocomposites exhibit novel optical, electrical, and magnetic properties compared with their pure metal oxide and present possibilities for several technological applications. Nano-sized oxide such as ZnO⁴, MgO, PbO⁵, NiO⁶, and Bi₂O₃⁷ have been added to (Bi,Pb)-2223 and exhibited enhancement in the transport critical current density (Jc). The size and element of nanoparticles are important to improve in Jc.

ZnO semiconductor is a promising material for applications. It is inexpensive with controllable electrical conductivity and environmentally friendly. Its properties have been extensively studied [e.g. 8]. ZnO has many applications such as for cytotoxicity⁹, antibacterial activities¹⁰, solar cells¹¹, gas sensors¹², and electrical and optical devices¹³,¹⁴. It has a wide band gap (3.37 eV) and large exciton binding energy (~ 60 meV), which allows efficient excitonic emission even at room temperature¹⁵,¹⁶.

ZnO has higher photocatalytic efficiency under UV irradiation and lower photocatalytic activity in the visible region. Therefore, significant efforts have been made to increase the ZnO activity in the visible region by metal or non-metal doped ZnO or ZnO composites¹⁷-¹⁹. Some elements could enhance the optical properties of ZnO while other dopants showed the opposite effect²⁰,²¹. This implies that a significant increase in the optical properties of ZnO would still be possible.

The doping of Ni in ZnO has important influence on the optical and electrical properties which present possibilities for applications in spintronics²²,²³. The NiO doped ZnO is one of the effective methods to enhance the optical and electrical properties of ZnO. A significant decrease in resistivity of ZnO/NiO nanocomposite thin film was observed compared with undoped sample and NiO dopant is suitable for photodiodes or UV detectors.

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The nickel acetate tetrahydrate ($\text{C}_4\text{H}_6\text{NiO}_4\cdot4\text{H}_2\text{O}$) were used as NiO source and the XRD analysis showed the NiO phase$^{24}$. Nickel (II) chloride hexahydrate were used as Ni source and the XRD showed the Ni$_2$O$_3$ phase$^{25,26}$. The nickel acetate hydrate ($\text{C}_3\text{H}_4\text{NiO}_2\cdot6\text{H}_2\text{O}$) has also been used to prepare pure Ni$_2$O$_3$ nanoparticles to remove toxic Cd(II) ion. The excess oxygen in the surrounding NiO$_3$ produces Ni vacancies which occupy the Ni$^{2+}$ sites and create Ni$^{3+}$ ions$^{23-25}$. In the reported work, the nickel nitrate hydrate ($\text{Ni(NO}_3)_2\cdot6\text{H}_2\text{O}$) was used as Ni$^{2+}$ source.

Silver as a metal nanoparticle is a good candidate for antimicrobial and biomedical applications. Doping ZnO with Ag improved the optical properties and can be used as optoelectronic devices$^{8,10,19,28}$. The improvement of photocatalytic activity of ZnO depends on the hindering of electron–hole recombination which is achieved by metal dopants such as Ag$^{25,30}$. An improvement in the electrical properties of Ag doped ZnO:Al was observed due to the enhancement in the crystalline quality$^{31}$. ZnO has also been prepared using the ultrasonic and wet chemical method$^{32}$.

A report on Ni-doped ZnO nanoparticles with 3.9, 8.3 and 12.4 wt.% showed that Ni ions are substituted in the ZnO lattice as evidenced from X-ray diffraction and UV–visible reflectance studies$^{33}$. In another report, X-ray diffraction and ICP-MS results confirmed the incorporation of Ni$^{2+}$ in Cd$_{1-x}$Ni$_x$O nanoparticles with $x = 0.047–0.163^{48}$.

ZnO nanopowder is a promising material for applications due to its size-dependent properties. Ni and Ag doping ZnO is one of the effective methods to enhance the optical properties of ZnO. It would be interesting to firstly, prepare Ni and Ag doped ZnO with particles size in the nanometer range. Then, combine ZnO with different molar ratio of Ni and Ag (1, 3 and 5 mol.%) and finally compare the properties of Ni-ZnO with Ag-ZnO nanopowders. In this work two series, i.e. Ni doped ZnO and Ag doped ZnO nanopowder samples were prepared by the sol–gel technique. The pure ZnO nanopowder was also prepared to compare with the doped samples. The influence of Ni and Ag on the crystalline structure and optical properties of ZnO was investigated. The phase and structure, and optical properties of Ni-ZnO and Ag-ZnO nanopowders were investigated by X-ray powder diffraction (XRD) and the UV–visible spectrophotometer, respectively. The samples were analyzed by FTIR spectrophotometer. The absorption, optical gap energy and crystalline size of all prepared samples were evaluated.

### Experimental details

Pure ZnO, Ni doped ZnO and Ag doped ZnO nanopowders were synthesized using the sol–gel technique as follows.

#### Preparation of ZnO nanopowder.

For pure ZnO nanopowder, a homogenous solution was prepared by dissolving 9.9163 g of zinc nitrate hexa-hydrate ($\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}$) (FLUKA, 99%), as zinc oxide source and 6.4041 g of citric acid anhydrous ($\text{C}_6\text{H}_8\text{O}_7$) (HIMEDIA, 99.7%) in de-ionized water (80 ml).

#### Preparation of Ni-ZnO and Ag-ZnO nanopowders.

Ni doped ZnO (Ni-ZnO) nanopowder was prepared by dissolving 9.9163 g of zinc nitrate hexa hydrate, 6.4041 g of citric acid anhydrous and nickel nitrate hexa hydrate ($\text{Ni(NO}_3)_2\cdot6\text{H}_2\text{O}$) (Fluka, 98%) as Ni source in de-ionized water (80 ml). Ag with ZnO (Ag-ZnO) nanopowders were synthesized using the same technique described for Ni-ZnO, except $\text{AgNO}_3$ was used as Ag source instead of $\text{Ni(NO}_3)_2\cdot6\text{H}_2\text{O}$.

The different molar ratios (0, 1, 3 and 5 mol.%) of $\text{Ni(NO}_3)_2\cdot6\text{H}_2\text{O}$ and $\text{AgNO}_3$ were chosen to prepare Ni-ZnO and Ag-ZnO nanopowders, respectively. The prepared solutions were stirred separately by a magnetic stirrer for 3 h and heated at 42 °C. The solutions were kept at room temperature for 24 h. The resulting solutions were stirred for another 1.5 h and heated at 72 °C for 48 h. Within the third day, the reaction mixtures were stirred for 1 h and heated at 92 °C until gels were obtained. The prepared materials were dried at 120 °C for 4 h in an oven and then ground for 10 min. The resulting powders were heat-treated at 450 °C for 6 h in a furnace.

#### Characterizations.

The crystal structure and phase of pure ZnO, Ni-ZnO and Ag-ZnO nanopowders were investigated by X-ray powder diffraction (XD-2/XD-3 with CuKα radiation; $\lambda = 1.5406$ Å) Fourier transform infrared (FTIR) spectrophotometer of the samples was recorded using FTIR-8400S. The absorption, optical gap energy and crystalline size of all prepared samples were evaluated.

The crystal structure and phase of pure ZnO, Ni-ZnO and Ag-ZnO nanoparticles with different molar ratio of Ni and Ag (1, 3 and 5 mol.%) and finally compare the properties of Ni-ZnO with Ag-ZnO nanopowders. In this work two series, i.e. Ni doped ZnO and Ag doped ZnO nanopowder samples were prepared by the sol–gel technique. The pure ZnO nanopowder was also prepared to compare with the doped samples. The phase and structure, and optical properties of Ni-ZnO and Ag-ZnO nanopowders were investigated by X-ray powder diffraction (XRD) and the UV–visible spectrophotometer, respectively. The samples were analyzed by FTIR Spectrophotometer. The absorption, optical gap energy and crystalline size of all prepared samples were evaluated.

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The optical properties of the prepared samples were investigated using UV–visible spectrophotometer (Varian, Cary 50) in the wavelength range of 200–1100 nm. The direct transitions band gap energies ($E_g$) were calculated by using the Tauc’s equation:

$$\alpha = B \left( \frac{h\nu - E_g}{h\nu} \right)^{1/2}$$

where $\alpha$ is the optical absorption coefficient, $B$ is a constant, $h$ is the Planck constant and $\nu$ is the wave frequency. The $\alpha$ of the samples was determined from the following equation:

$$\alpha = \frac{1}{d} \ln \frac{1}{A}$$

where $A$ is the absorbance and $d$ is the optical path length (1 cm).

The dislocation density $\delta$ was measured by the following equation:

$$\delta = \frac{1}{D^2}$$

**Results and discussion**

In this section we will discuss the XRD, FTIR and optical properties of the ZnO doped with Ni and Ag.

**XRD analysis.** Figure 1 shows the XRD patterns for ZnO and Ni-ZnO nanopowders in the range $2\theta = 25^\circ$–75$^\circ$. The peaks of the pure sample correspond to the ZnO hexagonal wurtzite structure (JCPDS file no. 36-1451). The ZnO hexagonal phase has typical peaks with Miller indices of (100), (002), (101), (102), (110), (103), (200), (112), and (201). The diffractograms of Ni doped ZnO also maintained the hexagonal structures of ZnO and no other crystalline phase was detected. The absence of any Ni associated peaks in the diffractograms signals the successful incorporation of Ni into ZnO crystal network as also reported in a previous report.

XRD patterns for pure and Ag doped ZnO are shown in Fig. 2. The peaks of ZnO were verified by the presence of hexagonal structure of ZnO phase. Besides, peaks associated with cubic structures of Ag phase were observed and comparable to JCPDS file no: 04-0783. The cubic Ag phase has peaks at (111), (200), and (220). The intensity of Ag peaks increased with increasing AgNO$_3$ amount. This indicated the presence of stable metallic Ag as secondary crystalline phase in the Ag-ZnO samples. The presence of Ag peaks in the XRD patterns of Ag-ZnO is in agreement with results in a previous report.

The significantly larger radius of Ag$^{+1}$ (0.126 nm) compared with Zn$^{+2}$ (0.070 nm) is the possible reason for the existence of the secondary crystalline phase in the Ag-ZnO samples. The difference between radius of Ag$^{+1}$ and Zn$^{+2}$ limits the solubility of Ag in Zn lattice site. Tables 1 and 2 show the 2$\theta$, hkl, phase ID and crystallite size (D) of Ni-ZnO and Ag-ZnO nanopowders as derived from XRD patterns in Figs. 1 and 2, respectively.
The average lattice parameters for pure ZnO were \(a = 3.2547 \text{ Å}, \quad b = 3.2547 \text{ Å}, \quad c = 5.2103 \text{ Å}, \quad \text{and} \quad c/a = 1.6009\) (Table 3). These values are consistent with the JCPDS file no. 36–1451 \(a = 3.2535 \text{ Å}, \quad b = 3.2535 \text{ Å}, \quad c = 5.2151 \text{ Å}, \quad \text{and} \quad c/a = 1.60292\). The was a slight variation of the lattice parameters with the presence of Ni and Ag from that of pure ZnO. That may be due to the successful dopant incorporation in Ni-ZnO and existence of microstructural strain from defects in Ag-ZnO35,39.

From the XRD data, the crystallite sizes \(D\) of Ni-ZnO and Ag-ZnO nanopowders were estimated from FWHM of all the peaks using the Scherrer’s equation (Eq. 3). For comparative purpose, Fig. 3 shows the average crystallite size of prepared samples as a function of Ni and Ag contents. The average crystallite sizes of the prepared samples were found to be in the nanometer range of 17–22 nm for Ni-ZnO and 19–26 nm for Ag-ZnO. By comparison, the average crystallite size of pure ZnO was 19 nm. Doping ZnO with 1 and 5 mol.% Ni produced broader XRD peaks and hence lower average crystallite sizes. However, ZnO doped with 3 mol. % Ni showed narrower peaks than pure ZnO suggesting the increment in average crystallite size and reduction in dislocation density35. The crystallite sizes of Ag-ZnO increased with increasing Ag content, whereas the average FWHM was decreased with increase in Ag. The crystallite sizes of Ag-ZnO were in good agreement with the results in

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The average crystallite size, lattice parameters, average FWHM and dislocation density of pure ZnO, Ni doped ZnO and Ag doped ZnO nanoparticles are shown in Table 3.

| Sample                  | D (nm) Avg | FHWM Avg (deg) | Optical Band gap (eV) | δ (nm−2) | a=b (Å) | c (Å) | c/a |
|-------------------------|-----------|----------------|-----------------------|----------|---------|-------|-----|
| ZnO                     | 19.13     | 0.4259         | 3.10                  | 0.0027   | 3.2547  | 5.2103| 1.6009|
| 1 mol.% Ni-ZnO          | 18.47     | 0.4581         | 3.05                  | 0.0029   | 3.2507  | 5.2096| 1.6026|
| 3 mol.% Ni-ZnO          | 21.67     | 0.3793         | 2.95                  | 0.0021   | 3.2547  | 5.2099| 1.6007|
| 5 mol.% Ni-ZnO          | 17.77     | 0.4697         | 3.00                  | 0.0032   | 3.2549  | 5.2156| 1.6024|
| 1 mol.% Ag-ZnO          | 19.95     | 0.4214         | 2.90                  | 0.0025   | 3.2667  | 5.2305| 1.6012|
| 3 mol.% Ag-ZnO          | 22.21     | 0.3612         | 2.00                  | 0.0020   | 3.2668  | 5.2276| 1.6002|
| 5 mol.% Ag-ZnO          | 25.63     | 0.3134         | 1.80                  | 0.0015   | 3.2668  | 5.2277| 1.6003|

Table 3. The average crystalline size, lattice parameters, average FWHM and dislocation density of pure ZnO, Ni doped ZnO and Ag doped ZnO nanoparticles.
which relates to the UV region. The absorption edges of doped ZnO with molar ratios of 1, 3 and 5 mol.% Ni were observed at 374 nm, 377 nm and 376 nm, respectively. The absorption edges for Ag-ZnO samples with molar ratios of 1, 3 and 5 mol.% Ag were observed at 379 nm, 387 nm and 390 nm, respectively. It appears that the absorbance in the UV band of both samples was higher, except for 1 mol.% of Ag in comparison with the pure ZnO. Among Ni–ZnO, the highest absorption was in small amount of Ni (1 mol.%) within the wavelength range of 300–550 nm. In Ag–ZnO series, a small amount of Ag (1 mol.%) exhibited a weak absorbance. However, the higher amount (5 mol.%) presented the highest absorption between 300 and 800 nm. This indicates that the absorption bands of Ag-ZnO (3 and 5 mol.%) in the visible region were wider compared to the pure and Ni doped ZnO. The sample with molar ratio of 1% Ni exhibited a strong absorption in the UV band and weak absorbance in the visible region. Therefore, it can be potentially used as sunscreens in commercial products.²¹
wavelength larger than 400 nm, the optical absorption was the highest with 3 and 5 mol.% Ag compared to other samples. For future work, these samples can be used as an efficient photocatalyst under irradiation with visible light of wavelength larger than 400 nm.

Figure 5. The optical absorption spectra of pure, Ni doped ZnO and Ag doped ZnO nanopowders.

Figure 6. The optical transmittance spectra of pure and ZnO doped with Ni and Ag nanopowders.

In Ag–ZnO samples, a small amount of Ag (1 mol.%) doped ZnO was highly transparent between 300 and 740 nm in comparison to the pure ZnO. Doping ZnO with 3 and 5 mol.% Ag decreased the optical transmission as compared to the pure ZnO. Ni–ZnO showed higher transparency in the visible regions greater than 480 nm.
and the lowest transparency in wavelength smaller than 480 nm in comparison to the pure and Ag doped ZnO. By comparing all samples, Ag–ZnO exhibited the highest transparency within wavelength smaller than 440 nm.

From Eq. (4) and plotting $(\alpha h \nu)^2$ versus the photon energy ($h \nu$), the value of energy gap ($E_g$) can be found by extrapolating the intercept of the curve to zero absorption in the photon energy axis. The band gap energy of pure ZnO nanopowder (3.1 eV) was less than that of bulk ZnO (3.37 eV). This reduction in the energy band gap agrees with those reported in the literature\textsuperscript{10,37}. The band gap energies of Ni–ZnO and Ag-ZnO nanopowders were smaller than that of pure ZnO nanopowder which may be due to the effect of Ni and Ag concentrations. The band gap energies of Ni–ZnO nanopowders varied between 3.1 and 2.95 eV for 1, 3 and 5 mol.% Ni, respectively. The inset of Fig. 7 shows the decreasing of energy gap of Ni-ZnO nanopowders compared to the pure ZnO.

![Figure 7. $(\alpha h \nu)^2$ versus the photon energy ($h \nu$) of pure and Ni doped ZnO nanopowders. The inset is the energy gap of samples as a function of Ni content.](image-url)

![Figure 8. $(\alpha h \nu)^2$ versus the photon energy ($h \nu$) of pure and Ag doped ZnO nanopowders. The inset is the energy gap of samples as a function of Ag content.](image-url)
The band gap energies of Ag-ZnO nanopowders were reduced as compared with the pure ZnO (Fig. 8). The band gap decreased with increasing Ag content. They were 2.8 eV, 2 eV and 1.8 eV for 1, 3 and 5 mol.% Ag, respectively. The band gap energies of Ag-ZnO are shown in the inset of Fig. 8.

For comparison purpose, Fig. 9 and Table 3 show the values of band gap energies of the samples as a function of Ni and Ag contents. The band gap energies of Ag–ZnO were smaller compared with that of pure ZnO and Ni-ZnO samples. The decrease in the band gaps of the samples is useful in optoelectronic devices. There are several factors for the decrease in the optical energy band gap such as grain size, carrier concentration, structural parameters and lattice strain and existence of defects or impurities.

Conclusions
The effect of Ni and Ag on the structure and optical properties of ZnO has been investigated. Pure ZnO and ZnO containing different molar ratio of Ni and Ag (0, 1, 3 and 5 mol.%) were prepared by the sol gel technique. The crystallite sizes of all samples were estimated by using the Scherrer’s equation and were in the nanometer range. The optical properties of the samples were determined by UV–visible spectrophotometer. Ni and Ag had different effects on the structure and optical properties of ZnO. The average crystallite size was 19 nm for pure ZnO. A slight decrease in the average crystallite size of Ni-ZnO was observed in comparison to the pure ZnO. Ni-ZnO also showed a smaller crystallite sized compared to Ag-ZnO. The average crystallite sizes were between 17 and 22 nm for Ni–ZnO and between 19 and 26 nm for Ag–ZnO. The band gap energy of pure ZnO was 3.1 eV. The doped samples exhibited better optical properties in comparison with pure ZnO. A slight decrease in the band gap energies of Ni-ZnO was observed in comparison to the pure ZnO. Ag-ZnO exhibited a higher decrease in the band gap energies than Ni-ZnO. Ni-ZnO showed better absorption in the UV band whereas Ag-ZnO exhibited better absorption in the visible light. The improvement of optical properties of ZnO depends on the type and amount of metal oxide dopants.

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Author contributions

S.A.-A., N.A.A.Y. and S.A.A.-A. designed, performed the experiments and analyzed the results. N.A.A.Y. wrote the draft of the manuscript. M.H.H.J. analyzed the XRD results. A.N.J. analyzed the optical results. R.A.-S. designed the research and wrote the final draft. All authors reviewed the final version of the manuscript.

Competing interests

The authors declare no competing interests.
