Enhanced Electrical and Optical properties of Al doped and ZnO nanoparticles for Optoelectronic Application: Eco-friendly Green Route

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Abstract: Optoelectronic materials have been developed greatly due to the wide usage of Liquid crystal displays, touch screens and light-emitting devices. In this work, a simple, eco-friendly green synthesis method has been adopted for the synthesis of pure and Al doped ZnO nanoparticles (1, 3 and 5 wt. %). Bio-extract was extracted from Citrus Aurantium peel. The structural, optical and electrical properties of the as-synthesized material were analyzed by X-ray diffraction, Scanning Electron Microscopy, UV-Visible spectroscopy and Hall Effect measurements. XRD spectra indicate the presence of hexagonal wurtzite structure. The crystalline size is decreased with increasing Al concentration. Scanning electron microscopy results indicate that the addition of Al changes the morphology from rod shape to platelets shape. UV-Visible results infer the shift in the band edge towards lower wavelength and the bandgap increases with Al concentration. Hall effect measurements reveals the enhanced carrier concentration in 5 wt% Al doped ZnO with the values of 1.3 X 10²¹ cm⁻³.

Keywords: Al doped ZnO, Bio-extract, Green Synthesis, enhanced optical and electrical property

1. Introduction
In the modern energy era, transparent conducting oxide electrode (TCO) material plays a very important role. TCO material possesses high electrical conductivity and optical transparency, hence it is widely used in optoelectronic devices. As of now, tin-doped indium oxide (ITO) is most commonly used TCO material for transparent electrodes due to its excellent electrical and optical properties ¹ ². But the main drawback of ITO is high cost and increasing demand for indium raw materials. Hence, Researchers are currently searching for an alternative to indium tin oxide. Nowadays, binary oxides such as CdO, SnO₂, In₂O₃, ZnO with dopants, and combinations of these binaries being used as a TCO material. Among all, Zinc Oxide (ZnO) is considered as a promising material for TCO and has attractive properties like wide bandgap (3.2eV) and a large exciton binding energy of 60 meV, low cost and environmental-friendly material. However, the main drawback of ZnO material is more sensitive to oxygen, which could be rectified by doping with III group elements. Work continues on improving the electrical and optical property of ZnO by doping Boron (B), Aluminum (Al), Gallium
(Ga). In these dopants, Al doping in ZnO is considerably more attraction due to its low ionic radius (Al\(^{3+}\) - 68 pm), superior electrical conductivity, low cost, and environmental friendly material \(^3\)\(^4\). In this regard, Lot of Research has been adopted to synthesize Al doped ZnO nanostructures. The noteworthy techniques are sol-gel, hydrothermal, sputtering \(^5\)\(^6\)\(^7\). Compared with the chemical and physical method of synthesis, the Green synthesis technique has significant advantages and possesses non-toxic and safe environmental friendly reagents. In this green synthesis technique, the bio-solvent extracted from the plant and fruit wastes are used. The bio-extract contains various phytochemicals, which act as reducing agents and used to synthesize metal oxides. Hence, in the present study, a green synthesis method was adopted to the synthesis of pure and different concentrations of Al doped ZnO material. The effect of Al concentration on the optical and electrical properties was analyzed.

2. Experimental
In this study, the bio-solvent was extracted from Citrus Aurantium peel and used for the synthesis of undoped and Al doped ZnO (1, 3 and 5wt %) material. Appropriate amounts of Zinc nitrate hexahydrate (Zn(NO\(_3\))\(_3\) 6H\(_2\)O) and Aluminum nitrate nonahydrate (Al(NO\(_3\))\(_3\) 9H\(_2\)O) were dissolved in 50 ml of distilled water. The bio-solvent was added to the solution by dropwise with constant stirring. The solution was heated at 60\(^\circ\)C for 2 h and followed by dried at 150\(^\circ\)C for 4 h. The dried powder was calcined at 500 \(^\circ\)C for 2 h.

2.1 Characterization
X-ray diffraction (XRD) pattern of undoped and Al doped ZnO were recorded using X’Pert PRO multipurpose PANalytical X-ray diffractometer. FESEM S-4800, Hitachi scanning electron microscope was used to record the morphology of the synthesized material. Elemental analysis was carried out using Thermo scientific NORAN system 7 X-ray Spectroscopy. Shimadzu UV 2450 spectrophotometer equipped with ISR-240A assembly was used to measure the optical property of the undoped and Al doped ZnO material. Electrical measurements were carried out using an HMS 5000 Hall Effect measurement, Ecopia, South Korea.

3. Results and Discussion
The structure of the undoped and 1, 3 and 5wt % Al doped ZnO material were carried out using X-ray diffraction analysis. Figure 1a shows the XRD pattern of undoped and 1, 3 and 5wt % Al doped ZnO material and the result confirms the hexagonal wurtzite structure of ZnO \(^8\). All the diffraction peaks were well indexed with standard ZnO, JCPDS No 36-1451. XRD result indicates that the crystallinity increases for Al 1 wt% doped ZnO and a further increase in concentration crystallinity was decreased. An enlarged version of XRD patterns is illustrated in Figure 1b, the XRD peaks (100), (002), and (101) were shifted towards lower angle, the observed peak shift suggest the incorporation of Al ions into the ZnO. Table 1 illustrate the lattice parameter values and crystallite size of undoped and 1, 3 and 5wt % Al doped ZnO material. Debye Scherrer equation is used to calculate the crystallite size of the synthesized material. The crystallite size decreases with increasing the Al concentration and very negligible changes in the lattice parameter were observed.

Table 1: Structural parameters of undoped and different concentration of Al doped ZnO

| S. No | Samples            | Crystallite Size (nm) | Lattice parameter (Å) | Volume (cm\(^3\)) |
|-------|--------------------|-----------------------|-----------------------|--------------------|
|       |                    |                       | a         | c         | c/a    |                       |
| 1     | JCPDS (36-1451)    |                       | 3.253     | 5.209     | 1.601  | 47.73                |
| 2     | Undoped ZnO        | 39.23                 | 3.240     | 5.1954    | 1.6035 | 47.23                |
| 3     | Al 1 wt.% doped ZnO| 38.85                 | 3.2477    | 5.2052    | 1.6028 | 47.54                |
| 4     | Al 3 wt.% doped ZnO| 34.88                 | 3.2505    | 5.2106    | 1.6028 | 47.68                |
| 5     | Al 5 wt.% doped ZnO| 30.28                 | 3.253     | 5.2144    | 1.603  | 47.79                |
Fig. 1a: X-ray diffraction pattern of undoped and different concentration of Al doped ZnO

SEM images of the as-synthesized undoped and Al doped ZnO are shown in Fig.2 (a-d). Rod shape morphology was observed for undoped and 1 wt% Al doped ZnO. However, with increasing the concentration of Al the rod shape morphology was changed to platelet morphology. The size of the platelets was low for 5 wt% Al doped ZnO. Figure 3 (a-d) shows the EDS spectra of the relative abundance of the material versus X-ray energy. EDS measurement confirms the formation of pure and Al doped ZnO. EDS analysis result reveals the presence of a stoichiometric amount of Al incorporated into the ZnO matrix. The negligible amount of carbon was present in the EDS spectra, it could be attributed to the carbon tape.

Fig. 2 (a-d) SEM images of undoped and 1, 3 and 5 wt. % Al doped ZnO respectively
The UV-visible absorption spectrum of undoped and different concentrations of Al doped ZnO is illustrated in Figure 5a. The absorption spectra indicate that the band edge is shifted towards lower wavelength and the blue shift with increasing Al concentration indicates the change in crystallite size. The bandgap of the material is calculated using the Tauc plot and the calculated bandgap values are 3.07, 3.1, 3.16 and 3.2 for undoped and Al doped ZnO respectively. The slight increase in bandgap with Al doping could be attributed to the higher carrier density. 

![Fig. 3 (a-d) EDS mapping of undoped and 1, 3 and 5 wt. % Al doped ZnO respectively](image)

![Fig. 4a Absorbance spectra b) Tauc plot of undoped and 1,3and 5 wt. % Al doped ZnO respectively](image)
Table 2 Electrical properties of undoped and different concentration of Al doped ZnO

| Sample                  | Carrier concentration (cm\(^{-3}\)) | Sheet Resistance (Ω/square) | Mobility (cm\(^2\)/Vs) | Hall coefficient (cm\(^3\)/C) |
|-------------------------|-------------------------------------|-----------------------------|-------------------------|-------------------------------|
| Undoped ZnO            | -3.6 X 10\(^{18}\)                 | 66650                       | 0.8898                  | -1.8621                       |
| 1 wt.% Al doped ZnO    | -1.12 X 10\(^{19}\)               | 12580                       | 0.2799                  | -0.55651                      |
| 3 wt.% Al doped ZnO    | -9.05 X 10\(^{19}\)               | 12524                       | 0.2297                  | -0.06894                      |
| 5 wt.% Al doped ZnO    | -2.17 X 10\(^{21}\)               | 12517                       | 0.1102                  | -0.00287                      |

The electrical properties of the undoped and Al doped samples are shown in Table 2. All the samples show n-type conductivity. The table shows that the charge carrier density increases with Aluminum concentrations and 5 wt% Al doped ZnO exhibit enhanced electron concentration of \(-2.17 \times 10^{21}\) cm\(^{-3}\). Introducing Al increases the free electron density by substituting Zn ions with Al ions which provide extra free electron. The Al\(^{3+}\) ions substitute Zn\(^{2+}\) ions resulting in the production of one free electron for every Zn\(^{2+}\) ions which improves the conductivity.

4. Conclusions

A green synthesis process using Citrus Aurantium peel is demonstrated for the synthesis of undoped and different concentration of Al doped ZnO. XRD results confirm the formation of hexagonal wurtzite structure and with increasing Al doping the crystallinity is decreased. SEM result shows rod shape morphology and with Al concentration, the morphology changes from rod to platelets shape. Al doping increases the bandgap and the blue shift in the band edge was attributed to the Burstein mass shift which increases the Fermi level of the conduction bands. Hall effect measurement result indicates Al doping increases the conductivity of ZnO and the Al doped ZnO could be an excellent choice as a suitable transparent conducting oxide material.

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