Structural and optical properties of colloidal InZnO NPs prepared by laser ablation in liquid

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Abstract. In the current work, colloidal of InZnO NPs were produced by pulsed laser ablation in liquid (PLAL) method. The effect of indium content on the structural, morphological and optical of the InZnO NPs was confirmed by Fourier transform infrared spectroscopy, Scanning electron microscopy, and UV-visible spectroscopy. The FTIR spectra showed the presence of the metal-oxide bond. The SEM exhibit different morphological aspects according to the (In/Zn) ratio. The optical transmittance of InZnO NPs has high value around 70 % in the visible region and the band gap value was varied between 3.29 to 3.25 eV.

1. Introduction
Transparent conducting oxides (TCO) like In$_2$O$_3$, SnO$_2$, and ZnO, have been most studied [1, 2]. Indium is an expensive and rare element, pure and doped ZnO films are investigated as an alternate candidate. Furthermore, these compounds are inexpensive, abundant, nontoxic and offer noticeably high chemical and thermal stabilities [3]. Because of that reason, ZnO is a promising material for various technological applications like electro-luminescent displays [4], heated mirrors [5], Schottky diodes [6], solar cells [7], and chemical sensors [8]. N-type ZnO with wide bandgap semiconductor ($E_g$=3.2 eV), its electrical conductivity is fundamentally via to intrinsic defects (interstitial zinc atoms, oxygen vacancies) and could be enhanced by adding group VII (F) or group III doping (B, Ga, In, Al) [9]. Doping type has been chosen to take into account the fact that the impurity size of the ionic radius mast is similar to that of the substituted ion, in order to avoid lattice distortions. The efficiency of the doping element is related to its electro-negativity and its ionic radius. Different approaches were utilized to generate indium doped zinc oxide IZO nanostructures like chemical vapor deposition [10], chemical method [11, 12], thermal evaporation [13, 14], sol-gel [15], pulsed laser deposition [16] and spray pyrolysis [17]. Among them, pulsed laser ablation in liquids (PLAL) is a simple and clean technique, and it does not need any pressure and temperature, also can utilize to produce a new compound of nanomaterials with the new phase [18, 19]. The size and shape of these nanoparticles depend on the ablation features such as energy, wavelength, number of pulse and pulse duration. [20]. In general, there is no data of In-doped ZnO via PLAL process. Therefore, here prepared colloidal of IZO utilized laser ablation in liquid and the influence indium doped on structural and optical properties were investigated.
2. Experimental details

The indium zinc oxide nanoparticles (IZO-NPs) were prepared via PLAL methods. A 1064 nm Q-switched Nd:YAG laser (9ns) was used to produce the nanoparticles. These techniques have two processes; the first step for ZnO-NPs production was accomplished via PLA of a Zn target (99.99% purity) immersed in a 3ml DIW. The second step is the doping process achieved by replacing the zinc target by Indium plate (99.99%) for the same surrounding liquid that contains the zinc nanoparticles previously. The pulse laser energy was constant in the range (80mJ) for a different ablation time that ranged (2, 3, 4 and 5) min.

To study the chemical assignment and bonds of undoped ZnO-NPs and doped with different concentration used Fourier Infrared Spectroscopy (FTIR) from (BRUKER-7613). The scan of the FTIR probes in ranging from (500 to 3000 cm\(^{-1}\)) for synthesized sample. The optical transmittance can be found via OPTIMA (SP-3000 Plus) double beam, These were achieved at ambient conditions utilizing quartz cell with (1 cm) optical path. Finally, the morphology was assessed using Scanning Electron Microscope (SEM) (type Tescan VEGA3, Czech).

3. Results and discussion

‘Figure 1’ the FTIR-spectrum of IZNPs are shown. The broad peaks around the region from 3000 to 4000 cm\(^{-1}\) show the presence of - OH is stretching vibrations. The peaks at 1635 cm\(^{-1}\) and 1636 cm\(^{-1}\) related to stretching vibrations of C-C. Also, several distinguishing bands got among a range of 500 - 800 cm\(^{-1}\)are owing to the existence of a bond (for In-O and Zn-O) [21]. While bands at 613cm\(^{-1}\), 615cm\(^{-1}\), 616cm\(^{-1}\), 627 cm\(^{-1}\)and 630 cm\(^{-1}\) for InZnO-NPs. These results agree with the reference [13, 14, 16].

![Figure 1](image)

**Figure 1.** FTIR spectrums of ZnO suspensions doping with different In concentration.

‘Figure 2’ shows views of zinc oxide with different concentration. The images show alter in morphology from hierarchical nanostructures, including the flower structure in (0%) ZnO with diameter ~ (3.9 µm) to nano-structures consist of flakes, droplets and slight nano-rods like structure with mean width ~ (100 nm) and mean length ~ (6 µm) for ZnO doped with 32%. In general, at ([In\(^{3+}\) = 8%], there are three major morphologies: (1) one of them is the one that shows clusters of
tiny particles with loose appearance, (2) the shard-like flake with flower, (3) the rods-shaped particles were observed (mean width ~187 nm, mean length ~12µm), and these continued to grow as the ablation time was increased. On indium doping the hierarchical ZnO nano-structures lack their morphology ([In^{3+}] = 12%) and cauliflower-like structure has appeared. For ([In^{3+}] = 21%), the rod's surface disappears and the conglomerates are composed of agglomerated tiny particles, and to structures with different morphology like flakes, droplets and small nano-rods ([In^{3+}] = 32%). These results are good agreement with data in reference [11].

Figure 2. SEM images of in doped ZnO structure with various concentrations.

‘Figure 3’ shows the transmittance spectra for undoped ZnO nanoparticles observed suspensions and doped with different indium concentration, which seen the broad peak around 300 nm for ZnONPs. With doping absorption, broad shifted a bit near lower wavelengths, which mean a red-shift in the transmission spectra [10, 22]. Also can notice, increased transmission intensity because light
scattering is high on an irregular surface of the in doped nano-structures, that increased as in concentration increased, that result is in good agreement with [12]. The high transmission in the UV wavelength was attached to the essential transmission and includes the transition of electrons among the band, this was used to locate the energy gap ($E_g$) in a semiconductor [12]. Doping with 21% and 32% show superior transparency over 70% in the entire visible-light in the NIR wavelength region, indicating that In content has negligible effects on the transmittance and the enhanced of visible-NIR range due to the improvement of crystallinity of IZO [13,15]. The higher transmittance at 32%, which indicates good homogeneity [23].

Figure 3. UV-Vis. Transmittance spectra of ZnO-NPs suspensions (0%) with different In doping concentration.

‘Figure 4’ shows the direct band gap values were obtained by an extrapolation of the linear portion in a plot of $(\alpha h\nu)^2$ against $h\nu$, notes that the energy gap of ZnO-NPs suspensions before doping equal ($E_g = 3.29$ eV). While, after doping ZnO-NPs with different in concentrations, the value of the energy gap was decreased from ($E_g=3.28, 3.27, 3.26$ to $3.25$), which shown in ‘figure 3’, these results were good agreement with reference [10, 12, 15]. This shift was associated with the majority carrier concentration [12]. The band shifts noted among doping are owing to vagaries in nano crystal structure. Also, corresponding for the theory of “semiconductor – metal” transition, a $E_g$ reduction as the impurity is additional than the "Mott-critical" density [24] therefore, doping indicates to recognizable reducing of the gap. When In doped insert to the ZnO lattices, the specified edge states establish at the sites of doped, with a decrease of gap Refs [25, 26].
Figure 4. Optical band gap of ZnO-NPs suspensions (0%) with different doping concentration.

4. Conclusions
Good quality InZnO NPs were prepared using the pulse laser ablation in liquid method. The existence of metal-oxide (In-O and Zn-O) bond was identified from FTIR spectra. SEM studies have revealed that the surface morphology of the films with changed from hierarchical nanostructures with flower-like morphology in pure ZnO to rods after doping in (32%). The IZO nanoparticles showed an average optical transmittance around 70% in the visible region; meanwhile, the band gap value was decrease varied between 3.29 and 3.25 eV.

References
[1] Nouneh K, Oyama M, Diaz R, Abd-Lefdlil M, Kityk I V and Bousmina M 2011 J. Alloys and Compounds 509 5 2631-38
[2] Abd-Lefdlil M, Douayar A, Belayachi A, Reshak A H, Fedorchuk A O, Pramodini S, Poornesh P, Nagaraja K K and Nagaraja H S 2014 J. Alloys and Compounds 584 pp 7-12
[3] Hsu H C, Tseng Y K, Cheng H M, Kuo J H and Hsieh W F 2014 J. Crystal. Growth 261 520-5
[4] Yi L, Hou Y, Zhao H, He D, Xu Z, Wang Y and Xu X 2000 Displays 21 4 147-9
[5] Wang Z, Chen Q and Cai X 2005 J. Appli. Surf. Sci 239 3 262-7
[6] Park W I, Yi G C, Kim J W and Park S M 2003 J. Appli Phys 82 24 4358-60
[7] Contreras M A, Egaas B, Ramanathan K, Hiltner J, Swartzlander A, Hasoon F and Noufi R 1999 Research and applications, 7 4 311-6
[8] Wan Q, Li Q H, Chen Y J, Wang T H, He X L, Li J P and Lin C L 2004 J. Appli Phys 84 18 3654-6
[9] Klaus E, Andreas K and Bernd R 2008 Transparent Conductive Zinc Oxide: Basics and Applications in Thin Film Solar Cells, Springer
[10] Tang K, Gu S, Liu J, Ye J, Zhu S and Zheng Y 2015 J. Alloys and Compounds 653 643-8
[11] Sharma M and Jeevanandam P 2014 J. Chemistry 53A 561-5
[12] Chava R K and Kang M 2017 J. Alloys and Compounds 692 pp 67-76
[13] Sugumaran S, Ahmad M N B, Jamlos M F, Bellan C S, Pattiyappan S, Rajamani R and Sivaraman R K 2015 Optical Materials 49 348-56
[14] Sugumaran S, Ahmad M N B, Jamlos M F, Bellan C S, Chandran S and Sivaraj M 2016 Optical Materials 54 pp 67-73
[15] Kim M S, Yim K G, Kim S, Nam G, Lee D Y, Kim J S, Kim J S and Leem J Y 2012 Acta Physica Polonica-Series A General Physics 121 1 217
[16] Fang H W, Hsieh T E and Juang J Y 2014 Solar Energy Materials and Solar Cells 121 176-81
[17] Shinde S S, Shinde P S, Bhosale C H and Rajpure K Y 2008 J. Physics D: Applied Physics 41 10 105109
[18] Khashan K S and Mohsin M H 2015 Surface Review and Letters 22 4 1550055
[19] Khashan K and Abbas S F 2016 International Journal of Modern Physics B 30 14 1650080
[20] Hamad A H, Khashan K S and Hadi A A 2016 In Applications of Laser Ablation-Thin Film Deposition Nanomaterial Synthesis and Surface Modification InTech.
[21] Bheeman D, Sugumaran S, Mathan R, Sivanesan D and Bellan C S 2014 Nanoscience and Nanotechnology 6 6 457-63
[22] Lee M Y, Song M K, Seo J H and Kim M H 2015 J. Appli Phys 54 6 065201
[23] Thomas R and Dube D C 2000 J. Appli Phys 39 4R 1771
[24] Wander A, Schedin F, Steadman P, Norris A, McGrath R, Turner T S, Thornton G and Harrison N M 2001 Physical review 86 17 3811
[25] Morales A E, Zaldivar M H and Pal U 2006 Optical Materials 29 1 100-4
[26] Mehra S, Bergerud A, Milliron D J, Chan E M and Salleo A 2016 Chemistry of Materials 28 10 3454-34