Structural, Optical, Morphological Properties of ZnO Nanoparticle/ZnO Nanorods

Dhufr Hadi Al-Weally¹, Araa Mebdir Holi ¹ and Asla Abdullah AL-Zahrani ²

¹Department of Physics, College of Education, University of Al-Qadisiyah, Al-Diwaniyah, Al-Qadisiyah 58002, Iraq
²Imam Abdulrahman bin Fiasal University, Eastern Region, Dammam, Saudi Arabia
Email: araa.holi@qu.edu.iq

Abstract. ZnO nanoparticles/ZnO nanorods (ZnO NPs/ZnO NRs) were prepared via Chemical methods: dip-coating/ sol-gel method (DC/SG-M) and hydrothermal method (HT-M). The structure of ZnO NPs/ZnO NRs was studied utilizing X-ray diffraction (XRD). The UV-Visible spectrometer was used to analyze the absorption spectra. Surface morphology of prepared ZnO NPs/ZnO NRs was studied via field-emission scanning electron microscopy (FE-SEM). Starting with (XRD) study, it confirms that the prepared ZnO NPs/ZnO NRs has the hexagonal phase structure. Moreover, the average crystallite size of the ZnO NPs/ZnO NRs was 22.7 nm and 51.5 nm, respectively. FE-SEM result reveals that the prepared ZnO NPs/ZnO NRs samples have shown the nanoparticles-shape of the first prepared layer via dip-coating and radial hexagonal-shape of the second prepared layer via the hydrothermal method. The absorption spectra of ZnO NPs and ZnO NRs were around at (382 and 400) nm with the estimated direct band gaps energy were (3.24 and 3.10) eV, respectively.

1. Introduction

A question always asks: What is makes Zinc oxide (ZnO) an attractive competitor material among a variety of materials in the fabrication of the devices of optoelectronic applications? ZnO has a direct and wide bandgap 3.37 eV at room temperature [1], large piezoelectric constants [2], high thermal conductivity [3], room temperature mobility of 205 cm² V⁻¹ s⁻¹ [4], with high free exciton binding energy of 60 meV [5], large non-linear optical coefficients[6], strong luminescence [7], and strong sensitivity [8], all these properties made it an adaptable material and has applications in solar cells [9], photoelectrochemical electrodes [10], photocatalysts [11], sensors [12], piezoelectric devices [13], ultraviolet laser diodes [14], and electroluminescent application [15]. There are different techniques to prepare ZnO nanomaterials via solvothermal and hydrothermal methods. Dip coating/ sol-gel method (DC/SG-M) is commonly employed to obtain different functional oxide-film types. In addition, the mixture of metal salt with water under temperature effect has represented the hydrothermal method (HT-M) that is one of the most used methodologies and with low cost for the synthesis of nanometers. In this study, the ZnO nanoparticles/ZnO nanorods were prepared via dip coating sol-gel and hydrothermal methods and tested for their structural, optical properties and morphological surface were investigated.
2. Synthesis and characterization

The first step involves seed layer deposition. It was deposited onto an ITO glass substrate via sol-gel-dip coating method. The sol-gel solution of the coating was prepared by mixing 0.2 M zinc acetate-2-Hydrate [Zn(CH₃COO)₂·2H₂O] and 0.2 M diethanolamine NH(CH₂CH₂OH)₂ and the mixture solution was stirred for 30 mins at 60 °C to get a homogeneous and colloid solution which was aged overnight. After that, the dip-deposition was done by dipping the ITO glass substrates on the prepared solution. Finally, the ZnO NPs/ITO were annealed at 350 °C for 1 hour.

The second step includes hydrothermally deposition of ZnO nanorods. It was sitting up with mixed aqueous solution of 0.04 M zinc nitrate-6-Hydrate [Zn(NO₃)₂·6H₂O] and 0.04 M hexamethylenetetramine [HMTA, C₆H₁₂N₄]. After that, the ZnO NPs/ITO as seed layer samples were immersed in the prepared mixture solution at 90 °C for 4 h. Subsequently, these samples washed with deionized many times to remove the residual materials. Then, the ZnO NRs/ZnO NPs/ITO were annealed at 350 °C for 1 hour.

The structure and phases of the samples were analysed by X-ray diffraction (Shimadzu 6000 diffractometer) using CuKα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The absorbance spectra of the prepared samples were measured using (Shimadzu 1800/spectra photometer). It was recorded using plain ITO as a reference electrode in the range between 300 to 1100 nm. The morphology of the samples was obtained from field emission scanning electron microscopy (FESEM) using (FEI Nova NanoSEM 450) and operated at 10 keV.

3. Results and discussion

3.1 Structural Analysis

Fig.1 shows XRD patterns of the ITO glass, ZnO NPs/ITO, ZnO ZnO NPs/ZnO NRs/ITO samples scanned in 2θ range from 20° to 70°. Numerous of Bragg reflections are detected initiating from the prepared ZnO NRs were higher than and ZnO NPs samples. The peaks detected at values of 20 correspondence to the lattice plane as shown in Table. 1, which indicates that ZnO has wurtzite hexagonal structure of both samples. All the peaks are matched with standard ITO glass indexed as cubic (JCPDS card no. 039-1058) or to bulk ZnO, which could be indexed as the hexagonal wurtzite structure of ZnO (JCPDS card no. 003-0888). The crystallite size (D) of the prepared samples can be calculated by using Debye-Scherrer’s formula: \( D = \frac{0.9\lambda}{\beta \cos \theta} \). The crystallite size of prepared samples is found to be 22.7 nm and 51.5 nm for ZnO NPs and ZnO NRs, respectively, which are in the order of nanosize.

| hkl  | ZnO NPs/ITO | ZnO NRs/ZnO NPs/ITO |
|------|-------------|---------------------|
|      | (100)       | (002)               | (101) | (100) | (002) | (101) |
| 2θ (deg.) | 34.356 | 31.797 | 34.412 | 36.206 |
| d-spacing (nm) | 2.6103 | 2.8111 | 2.6026 | 2.4787 |
| FWHM (deg.) | 0.1812 | 1.4128 | 0.1613 | 0.4054 |
3.2 UV-Vis spectral analysis

The inset of the Fig. 2 displays the UV-Vis absorption spectra of ZnO NPs and ZnO NRs. It shows the optical absorption edge of ZnO NPs/ITO and ZnO NPs/ZnO NRs/ITO that is detected at around 382 nm and 400 respectively. Fig. 2 shows the band gap estimated 3.24 eV for ZnO NPs/ITO that is slightly varied than the ZnO NPs/ZnO NRs/ITO (3.10 eV). Consequently, the ZnO NPs/ZnO NRs/ITO is worthy optical and conducting properties compare to ZnO NPs/ITO due to the ZnO nanorods have more surface area than nanoparticles. Therefore, this property makes the nanorods shape greatest useful in numerous of applications.

Figure 1. XRD patterns (a) ITO glass and (b) (a) ZnO NPs/ITO and (c) ZnO NRs/ZnO NPs/ITO.

Figure 2. Band gap energy curves and UV-Vis spectra (shown in insets of the figure) of: (a) ZnO NPs/ITO and (b) ZnO NRs/ ZnO NPs/ITO.
3.3 Morphology Analysis

In Fig. 3 FE-SEM has been used to examine the surface morphology and to estimate the pure ZnO nanoparticles has obtained in uniform surface morphology. After growth the ZnO NRs the surface morphology of Fig.3 shows the radial hexagonal shapes of the particles are individually separated when compared to the pure ZnO NPs. As shown in the inset of Fig. 3 the average diameter of nanorods is ~ 90 ± 5 nm.

![Figure 3](image)

**Figure 3.** Field emission scanning electron microscopic images of the (a) ZnO NPs and (b) ZnO NRs at different magnifications.

4. Conclusion

In the current study, ZnO nanoparticles/ZnO nanorods were produced, which can be used in many applications. The XRD average crystallite size of ZnO nanoparticles and ZnO nanorods are 22.7 nm and 51.5 nm respectively with hexagonal phase. Optical absorption edges of ZnO NPs and ZnO NRs samples was practical at ~382 nm ~400 nm which corresponds to range in ZnO bulk. The calculated optical band gaps were found to be 3.24 eV and 3.10 eV for ZnO respectively. FE-SEM analysis has been utilized to examine the surface morphology and the obtained image has radial hexagonal shapes of the nanorods which are individually separated when compared to the ZnO nanoparticles.

References

[1] Dong H, Zhou B, Li J, Zhan J, Zhang L 2017 Ultraviolet lasing behavior in ZnO optical microcavities *Journal of Materiomics* 3 255-266.
[2] Molarius J, Kaitila J, Pensala T, Ylläjammi M 2003 Piezoelectric ZnO films by RF sputtering *Journal of Materials Science: Materials in Electronics* 14 431-435.
[3] Florescu D I, Mourokh L G, Pollak F H, Look D C, Cantwell G, Li X 2002 High spatial resolution thermal conductivity of bulk ZnO (0001) *Journal of applied physics* 91 890-892.
[4] Look D C, Reynolds D C, Sizelove J R, Jones R L, Litton C W, Cantwell G, Harsch W C 1998 Electrical properties of bulk ZnO *Solid state communications* 105 399-401.
[5] Bagnall D M, Chen Y F, Shen M Y, Zhu Z, Goto T, Yao T 1998 Room temperature excitonic stimulated emission from zinc oxide epilayers grown by plasma-assisted MBE *Journal of crystal growth* 184 605-609.
[6] Larciprete M C, Haertle D, Belardini A, Bertolotti M, Sarto F, Günter P 2006 Characterization of second and third order optical nonlinearities of ZnO sputtered films *Applied Physics B* 82 431-
[7] Shionoya S and Yen W H (ed) 1997 *Phosphor Handbook* By Phosphor Research Society (Boca Raton, FL: CRC Press).

[8] Nanto H, Sokooshi H and Usuda T 1991 Smell sensor using zinc oxide thin films prepared by magnetron sputtering *Solid-State Sensors and Actuators* 596-599.

[9] Zhou C, Ghods A, Yunghans K L, Saravade V G, Patel P V, Jiang X, Ferguson I 2017 ZnO for solar cell and thermoelectric applications. In Oxide-based Materials and Devices *International Society for Optics and Photonics* 10105 101051K.

[10] Mohd Fudzi L, Zainal Z, Lim H, Chang S K, Holi A 2018 Effect of Temperature and Growth Time on Vertically Aligned ZnO Nanorods by Simplified Hydrothermal Technique for Photoelectrochemical Cells *Materials* 11 1704.

[11] Ong C B, Ng L Y, Mohammad A W 2018 A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications *Renewable and Sustainable Energy Reviews* 81 536-551.

[12] Wei A, Pan L, Huang W 2011 Recent progress in the ZnO nanostructure-based sensors. *Materials Science and Engineering: B* 176 1409-1421.

[13] Bhatia D, Sharma H, Meena R S, Palkar V R 2016 A novel ZnO piezoelectric microcantilever energy scavenger: Fabrication and characterization. *Sensing and bio-sensing research* 9 45-52.

[14] Liu C Y, Xu H Y, Sun Y, Ma J G, Liu Y C 2014 ZnO ultraviolet random laser diode on metal copper substrate *Optics express* 22 16731-16737.

[15] Zhang S G, Zhang X W, Yin Z G, Wang J X, Dong J J, Wang Z G, Chow P P 2011 Improvement of electroluminescent performance of n-ZnO/AlN/p-GaN light-emitting diodes by optimizing the AlN barrier layer *Journal of Applied Physics* 109 093708.