Study the Characteristics Optical and Structure properties of ZnO-Nanoparticles fabricated by Laser Ablation in Liquid

Ghufran. S. Jaber\textsuperscript{1}  
khawla S khashan\textsuperscript{1*}  
Maha Jamal Abbas\textsuperscript{2}

\textsuperscript{1}Division of Laser science and technology, Department of Applied Science, University of Technology - Iraq; 
\textsuperscript{2}College of Dentistry, Al-Mustansiriyah University 
*\textsuperscript{1}corresponding author: khawla_salah@yahoo.com

Abstract. Pulsed laser ablation in double distilled water has been used to fabricate zinc oxide (ZnO) suspension. Nd:Yag laser, was employed to get ZnO colloidal by immersed the zinc target in high purity water (DDW) with various laser energy at room temperature. The optical properties, the morphology and particle size of the synthesized ZnO colloidal were measured by using UV–visible absorption and scanning electron microscope. The result showed the spherical shape and homogenous structure of the ZnONPs colloidal. The extrapolation curve of the band gap set forth the redshift can be related to the quantum confinement effect or quantum size. The band gap curve clarifies the change in band gap as a function of particle size which in turn agrees with the effective mass model (EMM).

Keywords Pulse Laser ablation in liquid (PLAL), Zinc oxide, Nano-colloidal, Nd:Yag laser.

1. Introduction
Nanotechnology at the recent time forms the primary nerve that entered at many new devices with a wide range of applications in the fields of medicine, electronics and energy production [1-4]. The physical properties of materials at the nano-scale behave in a different way compared with bulk levels. The most important points to focus on are high surface-to-volume ratio and clean surface. Many techniques are using to fabricate ZnO nanoparticles colloidal such as spray pyrolysis method [5], micro emulsion method [6], hydrothermal method [7], chemical method [8], and pulse laser ablation in liquid [9]. PLAL technique is used to get metal, metal oxide and composite nanoparticles by simple and quick steps. This technique has a lot of advantages compared with other physical and chemical methods such as high purity, simple and clean setup and do not require a vacuum [10-12]. PLAL have ability to control the size of particles by control the laser parameter, making it the most flexible and promising technique. At 1960, was fabricated as thin films which used in active field in many applications as sensors, transducers and catalysts and other applications. Zinc oxide has good chemical properties, and thermally stable type semiconductor, large direct band gap about 3.37 eV at RT and sensitive to toxic and combustible gases [13]. From previous years, several studies have been reached to both productions as well as electronic and optoelectronic applications of nanostructured Zinc Oxide.
[14]. Installation of ZnO at nanostructure its quasi-one-dimensional structure, with diameters in the range (100nm), this make it a good scientific point of view. In this size range, are expected to pass interesting physical properties and pronounced coupling quite different from their bulk counterpart [15], all these properties in addition to a cheap and nontoxic material that can be used in medical and cosmetically fields where used in commercial skin protection (sun screen), paint, antibacterial reagents and drug delivery applications [16]. This work is dedicated for the fabrication of ZnONPs from a zinc target submerges in deionized water by using Nd: Yag laser, and study the effect of variation laser energy on the resulting nanoparticles in term of size and band gap.

2. Materials and methods

In order to synthesize ZnO nanoparticles by PLAL using a zinc bulk was used as target. It immersed in 3ml of double distilled water (DDW) at room temperature. The laser utilized for the ablated process is Q-switched pulsed Nd:YAG laser work at (1064 nm, 1Hz ) maximum energy up to 500 mJ per one pulse. Nd:Yag laser beam was focused by using a convex lens(20cm) the distance between lens and target is (5cm). The vessel was continuously rotated to minimize the target etching effect, for production homogenous nanoparticles. The ZnONPs colloidal samples prepared at different laser energy by fixing the number of pulses 100pulses and energy (100, 180 and 260) mJ. By the time, the laser pulses fall on the target, causing the liquid to splash and hear sound. Figure 1 expresses about the setup of formation ZnONPs colloidal besides, it induces material loss, for the flying droplets contain NPs. The source of splashing is ascribed to laser-induced shock waves [17]. Nanoparticle size and concentration, will lead to variation in the color of zinc oxide nanoparticle solution in DDW.

![Figure 1. The setup of formation ZnONPs colloidal](image)

3. Results and discussion

UV-visible absorption spectra of the ZnONPs prepared by PLAL were determined over the wavelength range of 200–1200 nm. Optical absorption of colloidal ZnONPs samples prepared at different laser energy are shown in figure 2. Figure 2(a) describes the amount of ablated material inside the solution by a laser ablation process. First the target was weighted before and after the laser irradiation for every preparation condition [18]. After drying the targets, the amount of ablated target mass (ΔM) was calculated in table 1. The graph display that the concentration ZnO NPs in the colloidal clarify step by step in increasing with the laser energy. Also can be seen in figure (2b), the absorption spectra have peaks centered at (250, 230 and 210) nm for the laser energies (100, 180 and
260 μJ respectively. The change in color with increasing the laser energy was due to the increase in the temperature and pressure leading to increasing the size of ZnO nanoparticles [19]. By increasing the laser energy get to large particle size that leading to absorbance versus wavelength curve shifts to red direction [20].

Figure 2. (A) Mass concentration of ZnONPs, (B) Absorption spectrum of ZnONPs at different laser energy

Table 1. The absorption peak values versus laser energy, and mass concentration calculation.

| Sample | Laser energy (mJ) | Absorption peak (nm) | Optical band gap (eV) | Particle size (nm) |
|--------|-------------------|----------------------|----------------------|-------------------|
| S1     | 100               | 250                  | 4.9                  | 18.48             |
| S2     | 180               | 230                  | 5.2                  | 19.51             |
| S3     | 260               | 210                  | 5.8                  | 27.49             |

The band gap energy obtained by the extrapolating curve is found to be approximately (4.9, 5.2 and 5.8)eV for (100, 180 and 260) mJ laser energy[21]. It is also evident that significant sharp absorption of ZnO indicates the mono-dispersed nature of the nanoparticle distribution. The average particle size in a nano-colloidal can be calculated from the absorption onset of UV-Vis absorption spectra by using effective mass model [22]. Tauc plot of (αhv)½ versus energy hv is plotted in Figure 3.

\[ \Delta E = \left( \frac{\hbar}{2Me^*} \right) \frac{\pi^2}{d^2} \]  

Where \( \Delta E \) is the shift in optical gap with respect to the bulk band gap, \( \hbar \) is the Plank’s constant, and \( m^* \) is the exciton reduced effective mass equal to 0.24 me. The particle size for different laser energy estimate in table2. The result showed ZnONPs direct band gap energy where the energy band gap is inversely proportional to the size of particle [23]. XRD patterns getting from ZnONPs colloidal prepared by laser ablation in liquid at different laser energy. The X-ray diffraction data were recorded by using Cu Kα radiation (1.5406 Å). The intensity data were calculated between 2θ at range (20–80°). The diffraction peaks at angles 20 of 31.34°, 37.39° and 47.51° correspond to the reflection from the (1 0 0), (1 0 1) and (1 0 2) crystal planes of the hexagonal wurtzite zinc oxide structure [6]. After that estimate the grain size by using Scherer equation, X-ray diffraction studies confirmed that the synthesized materials were ZnO colloidal diffraction peak agreed with the reported data. As shown in figure.4 the mean grain size determine by using the Scherer:
D = 0.89λ/βCosθ \quad (2)

Where D of the particles size, λ is the wavelength of (Cu Kα), β is the full width at the half-maximum (FWHM) of the ZnONPs line and θ is the diffraction angle [24]. As shown in table the particle size calculation and lattice strain by using xpert high score plus program.

**Figure 3.** Extrapolation curve for ZnONPs colloidal to determine band gap at different laser energy

| Sample | Particle size | Lattice strain |
|--------|---------------|----------------|
| S1     | 42.1          | 9.91           |
| S2     | 56.9          | 0.83           |
| S3     | 57.30         | 0.41           |
As shown in figure 4(Left), certainly in crystalline solid different materials defect and disorder happen and can be detected by diffraction effects (line broadening). By Scherrer method obtained to particle-size and strain present in the sample. The strain (ε) associated with the material can be determined by Williamson-Hall (W-H) analysis where the Bragg diffraction angle dependency as in the Scherrer equation. This dissimilarity allows the separation of reflection broadening when both small crystallite size and strain together exists. A plot of βcosθ against 4sinθ (which is a straight line) gives information about the strain and the particle size in the form of the slope. The perfect crystal may be defined as one in which all the atoms are at rest on their correct lattice positions in the crystal structure. Such a perfect crystal can be obtained, hypothetically, only at absolute zero [25]. The size of particles varies in a range at few tens of nanometers. As obvious the fabricated nanoparticles are almost spherical in shape and homogeneous. The size distribution of ZnONPs is nearly Gaussian type. The image shows agglomerates of small grain of some dispersed ZnO NPs. The different images showed change of the laser energy that’s lead to may change in the distribution and particle size. Where (A) 100 mJ is used the particle size tends lowering in numbers in solution compared with B (180mJ) and C (260mJ) these tend to increase in concentration. The ablation attached with light ablates the surface front layer without any melting effects (surface effect). The increase in laser energy leading penetrates deeply the Zinc target to increase the colloidal concentration [16].
Figure 5. SEM images and size distribution for the prepared ZnONPs prepared by PLAL at different laser energy (A 100mJ, B 180mJ and C 260mJ).

4. Conclusion
Fabricated of ZnO nanoparticles by PLAL technique was achieved. According to the effect of the laser energy on the properties of ZnONPs was examined. According to the paper results, the following important points were concluded:

- The increase in the laser energy yielded large size of nanoparticles with narrow size distributions which is indicated by the red shift indicated through UV-Visible absorption spectra.
- Increasing the value of laser energy leads formation of larger particle sizes, more spherical, homogeneous and broad size distribution as showed in SEM image.
- Confirmation of zinc oxide nanoparticles formation can be represented by the X-ray diffraction result confirmed the formation of cubic structure, the particle size from Scherer equation approved the change of particle size with laser energy.
- Employing higher pulse energy in ZnO nanoparticles synthesis leaded to an increase in the particle size and concentration inside the solution. This increase in size of nanoparticles leading to decrease in band gap values due to the quantum size effect.

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