Synthesis of ZnO nanoparticles in polyvinyl alcohol solutions using laser assisted synthesis in solution (LASiS) method

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Abstract. ZnO nanoparticles are widely studied because of their superior properties so they are widely used in various applications. Structural modification with the right synthesis method is the key to getting superior properties. In this experiment, Laser Assisted Synthesis in Solution (LASiS) method was used to synthesize ZnO nanoparticles. The LASiS method was carried out using a metal plate Zn as a target placed in a solution of polyvinyl alcohol (PVA) with different concentrations, namely 1%, 2%, 3% and 4%. This laser ablation has caused a solution of gray colloidal ZnO nanoparticles. Different PVA concentrations do not affect the color of the produced ZnO nanoparticle solution. The properties and structure of ZnO nanoparticles were characterized using UV-Vis spectrophotometer, Zetasizer spectrometer, and Transmission Electron Microscopy (TEM). The UV visible absorbance spectrum shows the maximum absorption characteristics of ZnO nanoparticles observed at a wavelength of 344 nm. The maximum absorbance value rises by increasing the concentration of PVA and reaching the maximum value at a concentration of 3%. These ZnO nanoparticles have a size around 80 nm. TEM analysis shows that ZnO nanoparticles have a spherical shape and have good crystallinity based on SAED measurements. This property is due to the role of PVA in the synthesis process.

1. Introduction

The engineering of nanoparticle have been widely developed and used in a variety of technological applications and fundamental research. In nanosized materials, the physical and chemical properties of the material depend on the particle size, which is different from the bulk of the material [1]. One of the most versatile nanomaterials in nanotechnology is zinc oxide (ZnO).

ZnO nanoparticles are functional materials that have been widely researched because of their superior properties so they are widely used in a variety of applications such as optoelectronics, catalysis, biomedicine, and sensors [1-4]. ZnO nanoparticles have a wide direct band gap of 3.37 eV, large excitation binding energy (60 meV), and their ability to absorb UV light at room temperature, therefore ZnO nanoparticles show excellent photocatalytic activity [5].

ZnO nanoparticles can be produced from various methods such as hydrothermal, co-precipitation, photochemical, and others [6-8]. Each synthesis method produces specific nanoparticle properties. Modification of properties and structures with the right synthesis method is the key to obtaining superior properties of ZnO nanoparticles. One of the method that can be used in the production of ZnO nanoparticles is a laser ablation method.
Laser ablation is a good method to produce nanoparticles in solution, known as the Laser Assisted Synthesis in Solution (LASiS) method. LASiS method is a simple method to produce nanoparticles without requiring a vacuum environment, minimal contaminants, and less or zero chemical contact [9-11]. The size and distribution of nanoparticles can change by controlling laser parameters and solvent environment [4]. The solvents that used in the ablation process can be polymers because the polymers can stabilize metal nanoparticles [12]. In this study, the modification of the properties of ZnO nanoparticles using a water-soluble polymer, namely polyvinyl alcohol (PVA) have been performed by the LASiS method. PVA has been widely used because of their properties such as biocompatible, non-toxic, durable, chemically stable, and inexpensive [13].

2. Materials and method
2.1. Preparation and synthesis of nanoparticles ZnO
ZnO nanoparticle synthesis was carried out by a Laser Assisted Synthesis in Solution (LASiS) method using Q-Switched Nd laser: YAG (Neodymium-doped Ytrium Aluminum Garnet) from Quantel with specifications of 1064 nm wavelength, 10 Hz repetition rate, 5 ns pulse duration and energy of 120 mJ/pulse.

Polyvinyl alcohol (PVA MW 11000-31000) solution was prepared by dissolving PVA powder into 100 mL of double deionized water. The concentration of PVA solution varies to 1%, 2%, 3% and 4%. After that, the PVA solution was heated using a magnetic stirrer at 80°C for 10 hours.

The target is a 2x2 cm Zn metal plate with 99% purity. Before ablation, the Zn metal plate was washed using double deionized water. Then the Zn metal plate was placed at the bottom of the glass filled with 5 ml of double deionized water. This procedure was repeated using a PVA solution with varying concentrations. The ablation process was done by focusing the laser beam on the Zn target using a convex lens with a focal length of 150 mm. During this process, the solution was stirred continuously so that the resulting ZnO nanoparticles are evenly dispersed. The ablation process was carried out for 30 minutes for each solution used.

2.2. ZnO nanoparticles characterization
All of the synthesized ZnO nanoparticles were characterized by using a UV visible spectrophotometer from JASCO V-570, Zetasizer spectrometer Malvern Instruments Ltd., Malvern, UK and transmission electron microscope TEM FEI Tecnai G2 20S-Twin. The absorption spectrum was measured for a wavelength range of 200-800 nm. The stability of ZnO nanoparticles was analyzed using Zetasizer software (DTS, nano series, version 7.11, Malvern, UK). Furthermore, molecular weight distribution of the nanoparticles was studied by calculating the polydispersity index (PDI). Transmission electron microscopy was used to characterize the morphology, size, and structure of the produced ZnO nanoparticles.

3. Results and discussion
Figure 1 shows a series of photos of PVA solutions with various concentrations before ablation (a) and ZnO nanoparticle colloids produced after 30 minutes of ablation. Visually, after ablation the solution becomes cloudy gray. Variations in the concentration of PVA solutions did not show differences in the color of ZnO nanoparticle colloids.

The optical absorption spectra of ZnO nanoparticle colloid are shown in Figure 2. This absorption spectrum is measured after 1 hour of ablation process. At the wavelength of 273 nm there is an absorption peak from the PVA. This value corresponds to the experimental results of H.C. Haas et al. who has studied Vinyl Acetate polymerization which has the peak absorption characteristics in the ultra violet region at a wavelength of 280 nm [14].

The characteristic absorption peak of ZnO nanoparticles was observed at a wavelength of 344 nm. The peak value of characteristic absorptions is in accordance with the results of other researchers. ZnO nanoparticles prepared by the hydrogel method have plasmon resonance surface (SPR) characteristics around the wavelength of 364 nm [15], the laser ablation method in aqueous and ethanol solutions has
shown peak absorption at 360 nm [16] and in starch solutions has a peak absorption at 347 nm [17].

The optical properties of metal nanoparticles depend on the surface resonance of their plasmons. Plasmon occurs because free electrons in metal nanoparticles oscillate collectively. The magnitude of the peak intensity and width of plasmons depends on the size of the metal nanoparticles, the nature of the metal and the dielectric constant of the medium where the nanoparticles are located [15].

The relationship between the maximum absorption value of ZnO nanoparticles at 344 nm obtained from each sample with the concentration of PVA used during the ablation process is shown in Figure 3. The addition of PVA concentrations in water causes the peak value of the absorbance of ZnO nanoparticles to increase. This corresponds to the increasing number of nanoparticles obtained during the ablation time. This peak of absorbance reaches the maximum value when the PVA concentration is 3%. Further addition of the PVA concentration caused a decrease in the maximum absorption value of the spectrum of ZnO nanoparticles.

![Figure 1](image)

**Figure 1.** (a) PVA solutions with different concentration before ablation and (b) ZnO nanoparticles colloid generated by 1064 nm laser pulse.
Figure 2. Absorption spectra of ZnO nanoparticles prepared by LASiS in polyvinyl alcohol (PVA) solutions with different concentrations.

Figure 3. Maximum absorption at 344 nm as a function of PVA concentrations.

Zeta Potential (ZP) and Polydispersity Index (PDI) values for ZnO nanoparticles in double deionized water and PVA solutions with different concentrations are given in Table 1. Zeta potential values show the stability of ZnO nanoparticle colloids [17]. Zeta potentials in the range of ± 0-10 mV indicate that the colloids are highly unstable. For the range of values ± 10-20 mV and ± 20-30 mV, the colloid is in a moderate stable condition, and values above ± 30 mV are highly stable. ZnO
nanoparticles in double deionized water and PVA solution have a Zeta Potential value below ± 10 mV, which means the colloidal system is highly unstable as shown in Table 1. The concentration of PVA even affects the rate of formation of ZnO nanoparticles but does not influence the stability of existing colloids as shown by the Zeta Potential value which has no significant difference between all the solution parameters used for the ablation process. The average Zeta potential obtained is -4.22 mV.

**Table 1.** Zeta potential and dispersity of ZnO nanoparticles

| PVA Concentration | Zeta Potential (mV) | Polydispersity Index | Dispersity       |
|-------------------|---------------------|----------------------|------------------|
| 0                 | -5.16 ±3.98         | 0.82                 | Highly Polydisperse |
| 1                 | -3.14±3.24          | 0.94                 | Highly Polydisperse |
| 2                 | -6.23±5.37          | 1.00                 | Highly Polydisperse |
| 3                 | -2.70±2.80          | 0.94                 | Highly Polydisperse |
| 4                 | -3.88±3.14          | 0.98                 | Highly Polydisperse |

The size distribution of nanoparticles can be obtained by calculating the value of the polydispersity index (PDI). Nanoparticle systems that have PDI values <0.1 indicate high monodisperse properties. While the PDI value in the range 0.1-0.4 shows the distribution of nanoparticles is moderate polydisperse. If the value of the PDI> 0.4 system is highly polydisperse [16]. The calculation of PDI from the ZnO nanoparticles which are ablated in double deionized water and PVA solutions with different concentrations is given in Table 1. The PDI value of the ZnO nanoparticles for all of the samples has a value > 0.4. This value shows the sample has a highly polydisperse nature. The value of the polydispersity index of the ZnO nanoparticles was not affected by the conditions of the solution used during this ablation.

The TEM image of the ZnO nanoparticles prepared at different concentrations of PVA solution is shown in Figure 4. The figure shows that the ZnO nanoparticles for all of the PVA concentrations have an almost spherical shape. It can be seen that the size of the nanoparticles is not affected by the concentration of the PVA solution used. The resulting ZnO nanoparticles are not uniform in size, the largest size is around 80 nm. The highly polydisperse size distribution of the ZnO nanoparticles shown in TEM images is in accordance with the results of PDI calculations that have a value of >0.4.

**Figure 4.** TEM imaging for ZnO nanoparticles with (a) double-deionized water and different concentrations PVA (b) 1%, (c) 2%, and (d) 3%.
The selected area electron diffraction (SAED) pattern shows the characteristic ring of polycrystalline ZnO nanoparticles shown in Figure 5. The diffraction pattern shows that the existing ZnO nanoparticles have different crystal orientations. In Figure 5 shows that the ring of diffraction pattern diminishes with the increasing concentration of the PVA solution. These results show that the crystallinity of ZnO nanoparticles decreases and changes towards more amorphous. Concentration of the PVA solution affects the crystallinity of the ZnO nanoparticles produced. Increasing the concentration of PVA solution causes the rate of formation of ZnO nanoparticles to increase so that the crystallinity of the formed nanoparticles decreases, this corresponds to the results of the absorbance spectrum of the ZnO nanoparticles obtained.

Figure 5. SAED pattern of ZnO nanoparticles with (a) double-deionized water and different concentrations PVA (b) 1%, (c) 2%, and (d) 3%

4. Conclusion
ZnO nanoparticles have been successfully prepared by the LASiS method in the solution of double-deionized water and polyvinyl alcohol. The characteristic absorption peak of ZnO nanoparticles was observed at a wavelength of 344 nm. The value of the maximum absorbance is higher with increasing PVA concentration and reaching the maximum value at 3% PVA concentration. The resulting ZnO nanoparticles are not uniform in size with spherical morphology, the largest size is around 80 nm. ZnO nanoparticles in double deionized water and PVA solution have a Zeta Potential value below ±10 mV, which means the colloidal system is highly unstable. The PDI value of the ZnO nanoparticles for all of the samples has a highly polydisperse nature. The crystallinity of ZnO nanoparticles decreases with increasing PVA concentration.

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