Article **ECORFAN-Ecuador Journal**
June 2017 Vol.4 No.6 18-29

Synthesis and characterization of ZnO nanoparticles prepared by pulsed laser ablation in different liquid medium

GARCÍA-GUILLÉN, Grisel[1]*†, GARCÍA-QUIÑONEZ, Linda V.[1], GONZÁLEZ-GARZA, Jorge Oswaldo[1] and SHAJI, Sadasivan[2]

[1]*Universidad Politécnica de García, Calle Porfirio Díaz No. 106, Col. Centro Villa de García (CASCO), C. P. 66000, García, Nuevo León, México*
[2]*Universidad Autónoma de Nuevo León, Av. Pedro de Alba s/n, Cd. Universitaria, San Nicolás de los Garza, N. L.*

Received February 18, 2017; Accepted June 19, 2017

Abstract

Zinc oxide nanoparticles were prepared by pulsed laser ablation of zinc metal target using different liquid medium, distilled water and 2-propanol. Ablation was carried out using 532 nm and 1064 nm output from a pulsed (10 ns, 10 Hz) Nd:YAG, separately. Analysis of the morphology, crystalline phase, elemental composition and optical properties were done using Transmission Electron Microscopy (TEM), X-Ray Photoelectron Spectroscopy (XPS) and UV-Visible absorption. TEM analysis showed that a change in liquid medium and laser wavelength resulted in ZnO and Zn(OH)2 nanoparticles with different sizes and morphologies. XPS results confirmed the compositions and chemical states of these nanoparticles. The results of this work demonstrated that by varying the liquid medium, the structure, composition, morphology and optical properties of the nanomaterials could be modified during pulsed laser ablation in liquid.

Pulsed Laser Ablation, Semiconductor, Nanomaterials, Zinc Oxide

Citation: GARCÍA-GUILLÉN, Grisel, GARCÍA-QUIÑONEZ, Linda V., GONZÁLEZ-GARZA, Jorge Oswaldo and SHAJI, Sadasivan. Synthesis and characterization of ZnO nanoparticles prepared by pulsed laser ablation in different liquid médium. ECORFAN Journal-Ecuador. 2017, 4-6:18-29.

*Correspondence to Autor (E-mail: grisel@upg.com.mx)
† Researcher contributing as first author.

1. Introduction

Zinc oxide is a semiconducting material with optical energy band gap of 3.3 eV, also it is considered as an important material due its optical properties, electrical conductivity and piezoelectricity (Djurisic & Leung, 2006; Singh, Swarnkar, & Gopal, 2010). ZnO have been investiged due its applications in photovoltaics, photonics, light emitting devices, photo detectors, transparent conductive films, etc. (Francis B. Dejene, 2011). Nanostructures of ZnO have been synthesized by different chemical methods, such as solvothermal (Dev, Kar, Chakrabarti, & Chaudhuri, 2006), thermal evaporation (Pan, Dai, & Wang, 2001), sol-gel synthesis (Haase, Weller, & Henglein, 1988), chemical vapor deposition (Gorla et al., 1999; Song et al., 2013).

However, chemical methods involve the generation of chemical by-products, so, an alternative synthesis method to produce NPs colloids without impurities is Pulsed Laser Ablation in Liquid (PLAL) (Amendola & Meneghetti, 2009). In PLAL, a solid target is submerged into liquid medium; a high energy laser beam interacts with the solid target surface forming a plasma plume.

The chemical species inside of plasma plume are subjected to a nucleation and condensation processes which occur in the expanding plasma plume allowing nanoparticles growth in the liquid (Zeng et al., 2012). Nanorings of SiC have been synthesized by PLAL irradiating a Si target in ethanol. The proposed growth mechanisms are based on the plasma formation following by the reaction between the high active species and the carbon species from ethanol molecules allowing the nucleation and growth of SiC rings nanostructures (Yang et al., 2012).

However, the proposed mechanisms are under investigation because they are strongly depend of the experimental conditions, target and liquid medium properties, such as pulse duration, laser beam energy pulse, laser beam focusing, repetition rate, the presence of surfactant molecules in the liquid medium, the optical properties of the target, etc. (Itina, 2011).

Therefore, the present work takes into account the pulsed laser ablation of a Zn target in distilled water and 2-propanol using two laser wavelength from a Nd: YAG output to study the effect of liquid as well as laser wavelength on the size, morphology and structure of the laser ablation products. TEM analysis showed that a change in the liquid medium resulted in different morphologies and sizes of the zinc nanomaterials. XPS results confirmed that the NPs obtained were that of ZnO and $Zn(OH)_2$ for the laser ablation.

1.1 Justification

The advantages of using PLAL as synthesis method for semiconductor nanomaterials are that it is a simple experimental technique without the use of toxic chemical precursors to control the growth of the colloids and it can be applied in pure water or in a biologically compatible aqueous solution. However, the are some limitations such as controlling the average size distribution and the rate of ablation, also, the start-up costs due to the laser equipment, materials and optics supplies can be excessive.

Therefore, considering that the high costs are presented at the initial step, and the laser device, optical and raw materials supplies are available, the synthesis of nanomaterials by PLAL could be improved by the systematic studies on the effect of the adjustment of laser processing and experimental ablation parameters, resulting in an affordable synthesis method.

ISSN-On line: 1390-9959

1.2 Problem

Up to date, there have been substantial interests in the preparation, characterization and application of semiconductor materials at the nanometer scale. As a consequence, the physical and chemical properties of semiconductor nanomaterials are intensively studied looking for their application in new technologies, such as photovoltaics, optoelectronics, sensors, light emitting devices, etc.

There are chemical methods which are reliable and cost effective, allowing better control on the shape and size of the semiconductor nanoparticles by functionalization with different organic capping ligands. However, a huge disadvantage is the use of toxic chemical precursors, because the disposal of them implies that chemical methods represent an eco-undfriendly synthesis route. So, it is needed simpler and clean technologies for the preparation of nanostructures of metals, metallic alloys, semiconductors and polymers.

1.3 Hypothesis

The pulsed laser ablation of zinc metal target in distilled water and 2-propanol allows the production of ZnO nanomaterials having different size and properties.

1.4 Objectives

1.4.1 General Objecitve

The main objective is to synthesize and characterize nanomaterials of ZnO using pulsed laser ablation in liquid.

1.4.2 Specific Objectives

- To study the effects of laser ablation parameters (fluence and wavelength) on the formation and properties of the nanomaterials of ZnO by PLAL.
- To investigate the behavior of different liquid media (distilled water and 2-propanol) on the production of the nanomaterials as well as their structure, size distribution and morphology.
- To characterize the structure, morphology, composition and chemical states of these nanomaterials using various characterization techniques.
- To evaluate the optical absorption properties of these nanomaterial colloids.

2. Background

An alternative to synthesize ZnO nanostructures with different morphology, size, structure and optical properties is PLAL, a simple environmental friendly method. It is possible to vary some ablation conditions, such as liquid medium, pulse width and energy fluence in order to study the final properties of the as-prepared ZnO nanomaterials.

Zn metal and ZnO powders targets have been ablated in different liquid media, SDS, distilled water and 2-propanol (Hu et al., 2011; Liang, Tian, Tsuruoka, Cai, & Koshizaki, 2011; Shoutarou et al., 2010; Singh et al., 2010; Thareja & Shukla, 2007; Zeng, Cai, Li, Hu, & Liu, 2005; Zeng et al., 2010; Zeng et al., 2007) synthesizing ZnO nanomaterials with different morphologies.

Rods and flakes shaped ZnO nanoparticles, were formed by ablation of Zn metal and ZnO pellet in distilled water, respectively, showing both UV and visible emissions (Hu et al., 2011). Also, ZnO spherical nanoparticles have been obtained by ablation with 355 nm laser beam in distilled water and 2-propanol (Thareja & Shukla, 2007) and by ablation of ZnO chemical precursors in 2-propanol with a continuous laser (Shoutarou et al., 2010).

ISSN-On line: 1390-9959

Zn/ZnO nanoparticles were synthesized by ablation of Zn metal target in tetrahydrofuran using a high-power (25 W) picosecond-pulsed laser system, to achieve a control in their size and in the ablation efficiency by varying the repetition rate and laser fluence (Wagener, Faramarzi, Schwenke, Rosenfeld, & Barcikowski, 2011; Wagener, Schwenke, Chichkov, & Barcikowski, 2010). Moreover, a wavelength of 248 nm from a KrF excimer laser was used to irradiate a ZnO target in distilled water resulting in ZnO nanoparticles with ferromagnetic properties (Zhao, Huang, & Abiade, 2012).

ZnO quantum dots (1-8 nm) were synthesized through the size reduction by laser irradiation of ZnO hollow nanospheres (30 nm) originally prepared by PLAL and dispersed in distilled water. As the laser irradiation time was increased, the size of the ZnO hollow nanospheres was decreased, due to the laser fragmentation mechanism (Hu et al., 2012).

Laser parameters such as the laser wavelength, output power and fluence can be varied in order to study their effects on the size, morphology, structure and optical properties of the as-prepared ZnO nanostructures. In this way, w-ZnO and ε-$Zn(OH)_2$ composite nanoparticles (500 nm) with spherical and hexagonal shapes synthesized by pulsed laser ablation in water at different laser power outputs (800 mJ/pulse of 1064 nm and 400 mJ/pulse of 532 nm Nd:YAG), possessed an optical band gap of 3.1 eV (Lin, Shen, & Chen, 2011). Also ZnO nanoparticles were synthesized by PLAL in distilled water using the 1064 nm and 532 nm outputs from a Nd:YAG laser system at different fluences (Dorranian, Solati, & Dejam, 2012), where ZnO nanoparticles with smaller sizes by ablation with 532 nm and photoluminescence emissions at 335 nm and 375-377 nm.

3. Experimental Methodology

PLAL was the experimental technique used for the synthesis of ZnO nanomaterials. As described earlier, it is based on the pulsed laser ablation of a solid target in a liquid medium. In this study Nd:YAG pulsed laser system (Model LQ 929, Solar Laser System) having 10 ns of pulse width and 10 Hz of repetition rate, was used to irradiate a highly pure (99.99%) zinc metal plate as is shown in Figure 1.

3.1 Experimental design

The experimental parameters varied for the pulsed laser ablation were the energy per unit of area (energy fluence) and the liquid medium. The laser beam was focused using a convergent lens of suitable focal length. The energy fluence was estimated at different focusing conditions. Also, the liquid medium was changed in the presente work.

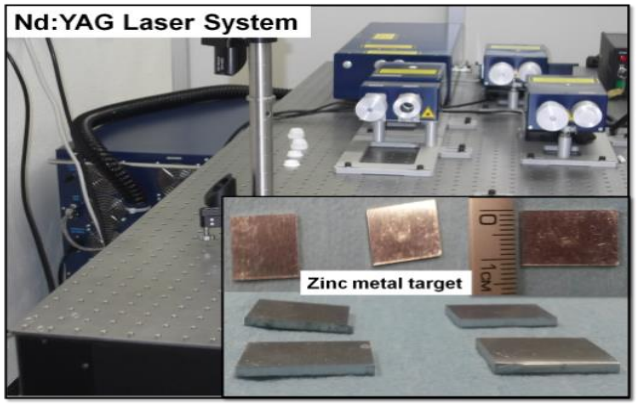

Figure 1 Nd:YAG laser and the Zn target used of the PLAL

Colloidal solutions of ZnO nanomaterials were synthesized through pulsed laser ablation of a highly pure (99.99%) zinc metal target, first in distilled water and after that in 2-propanol. The target was kept at the bottom of a glass vessel filled with 15 ml of liquid medium, 3 cm below the solution surface and was ablated during 5 minutes by the second harmonic (532 nm), and after, fundamental (1064 nm) of a Nd:YAG laser operated at 10 Hz with a pulse width of 10 ns.

ISSN-On line: 1390-9959

A laser energy meter (Model PM100D, Thorlabs Inc.) was used to monitor the output energy of the 532 and 1064 nm laser; they were 230 and 300 mJ/pulse, respectively. The laser beam was focused on the metal plate using a lens with a focal length of 20 cm and the estimated fluences were 3.9 J/cm^2 (532 nm) and 6.1 J/cm^2 (1064 nm).

3.2 Characterization

Drops of all of the coloidal solutions prepared at different ablation conditions were dried separately on carbon-copper grids to characterize their morphology, size and structure using Transmission Electron Microscopy (TEM, Model FEI Tital G2 80-300). All the samples were dried on conducting copper tapes to perform X-ray photoelectron (XPS) analysis (Thermo Scientific Inc. Model K-Alpha).

The analysis was done with monochromatized Al Kα radiation (E=1486.68 eV). The colloidal NPs solutions were subejectd to UV-Visible absorption analysis by a UV-Visible Spectrophotometer (Shimadzu UV-1800) in the wavelength range of 250-1000 nm. The results on morphology, structure, chemical composition and optical properties of nanomaterials obtained by pulsed laser ablation of zinc metal in different liquid medium were analyzed.

4. Results and Discussion

4.1 TEM Analysis

TEM images of the nanomaterials obtained by ablation using 532 nm and 1064 nm, at 3.9 and 6.1 J/cm^2, are shown in Figure 2 and Figure 3, respectively.

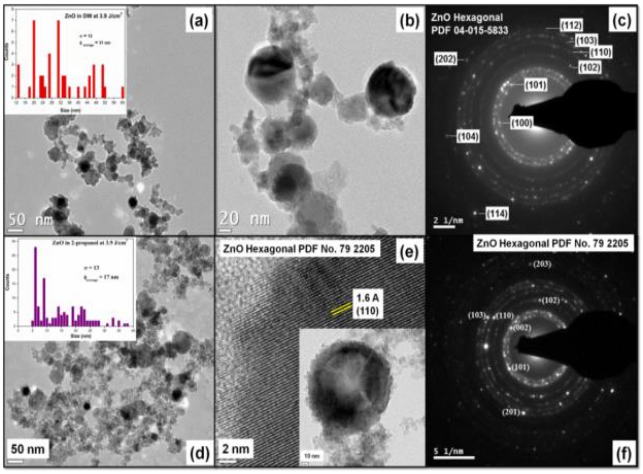

Figure 2 (a, b) TEM images and (c) SAED of ZnO colloids obtained by ablation in distilled water (532 nm, 3.9 J/cm^2). (d) TEM images, (e) HRTEM image and (c) SAED of ZnO colloids prepared by ablation in 2-propanol (532 nm, 3.9 J/cm^2)

Spherical and quasi-spherical nanoparticles which are linked as a chain (Figure 2a and 2b) were prepared in disitilled water at 3.9 J/cm^2. These nanoparticles do not follow a normal size distribution and their average size is 31 ± 13 nm (inset of Figure a). By ablation in 2-propanol at 3.9 J/cm^2 smaller spherical nanoparticles (17 ± 13 nm) are obtained which are agglomerated, as shown in Figure 2d.

The morphology of the products from the ablation at 6.1 J/cm^2 in distilled water is quasi spherical (Figure 3a and 3b) and they are smaller than those synthesized by ablation using 532 nm (10 ± 5 nm). Larger spherical nanoparticles were produced by ablation in 2-propanol using 1064 nm, as observed in Figure 3d and 3e.

ISSN-On line: 1390-9959

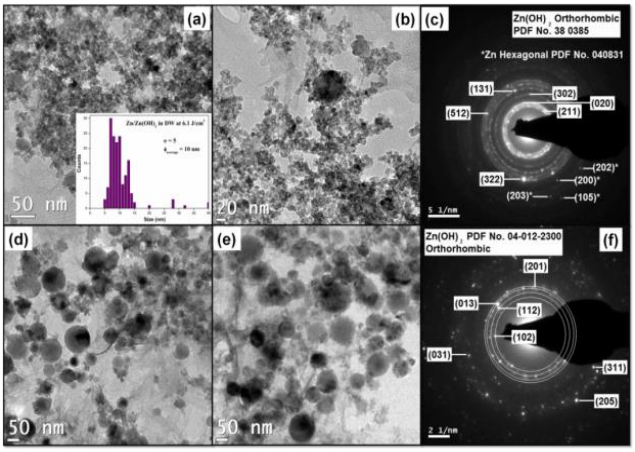

Figure 3 (a,b) TEM images and (c) SAED of Zn/$Zn(OH)_2$ nanoparticles obtained by ablation in distilled water (1064 nm, 6.1 J/cm^2). (d,e) TEM images and (c) SAED of $Zn(OH)_2$ nanoparticles obtained by ablation in 2-propanol (1064 nm, 6.1 J/cm^2).

The SAED (Selected Area Electron Diffraction) patterns of spherical nanoparticles prepared at 3.9 J/cm^2 are included in Figure 2c and 2f; the electron diffraction spots were indexed and the estimated lattice parameters 'd' are in agreement with the diffraction planes of ZnO Hexagonal phase (PDF #04-015-5833 and 79-2205, respectively). $Zn(OH)_2$ crystal phase was identified in the products from ablation at 6.1 J/cm^2 in distilled water and 2-propanol, as shown in Figure 3c and 3f. Also, the indexed diffraction rings of the nanoparticles obtained in distilled water correspond to Zn Hexagonal (PDF # 04-0831).

For both laser ablation products an EDX (Engergy Dispersive X-Ray) analysis was done. A spherical nanoparticle from the ablation in distilled water at 3.9 J/cm^2 is composed of 56.7 % and 43.3 % of zinc and oxygen, respectively (Figure 4a). Similarly, Figure 4b, shows that spherical nanoparticles in 2-propanol are composed of 37.6% zinc and 60.8 % oxygen.

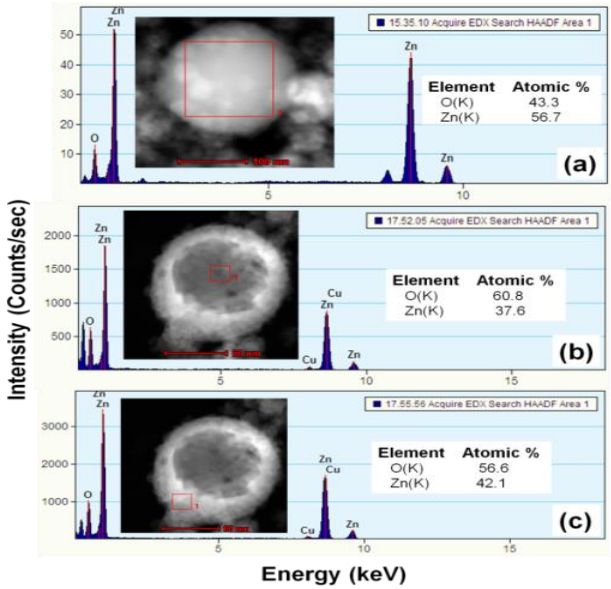

Figure 4 EDX analysis of ZnO colloids obtained by ablation in (a) distilled water and (b,c) 2-propanol (3.9 J/cm^2, 532 nm)

Figure 5a and 5b show that spherical nanoparticles obtained by the ablation using 1064 nm in distilled water were composed of 44.2% of zinc and 55.8% of oxygen.

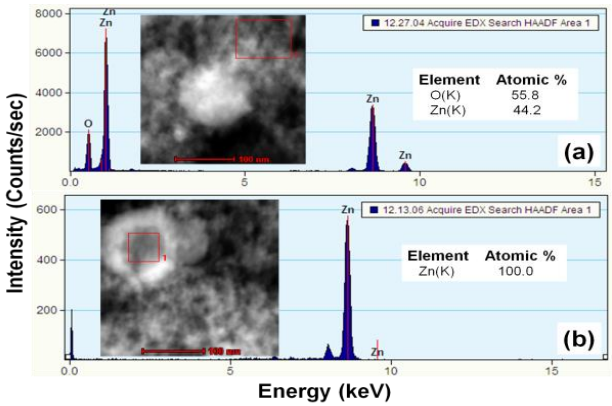

Figure 5 EDX analysis of Zn/$Zn(OH)_2$ nanoparticles prepared by ablation in distilled water at 1064 nm (6.1 J/cm^2)

The proposed laser ablation mechanism is thermal evaporation and the liquid media has an important role in determining the size or shape of the synthesized ablated particles.

ISSN-On line: 1390-9959

Due to the temperature gradient on both sides of the plasma-liquid interface, the highly active zinc clusters reacts with distilled water, leading to the nucleation and condensation of initial $Zn(OH)_2$, which can be decomposed to ZnO on the basis of the reactions (Liang et al., 2011; Zeng et al., 2005):

$$Zn(clusters) + 2H_2O \rightarrow Zn(OH)_2 + H_2 \quad (1)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (2)$$

As 2-propanol, $(CH_3)_2CHOH$, has an alcohol carbon atom and –(OH) functional group, attached to two other carbon atoms, it also tends to oxidize the highly reactive zinc ablated clusters. So, $Zn(OH)_2$ and ZnO nanomaterials can be produced by ablation of Zn metal target in both liquid media. Moreover, when the zinc clusters mix with the surrounding the initial parameters of the medium such as zinc cluster concentration chemical and physical properties, determine its following evolution.

As the distilled water has higher dipole moment than 2-propanol, their molecules tend to form a layer on the charged nanospheres, inducing an electrostatic repulsive force, which can prevent the aggregation of the as-produced nanoparticles (Lin et al., 2011; Rao, Podagatlapalli, & Hamad, 2014; Thareja & Shukla, 2007). Hence less agglomerated ZnO nanopaticles are produced by ablation of Zn target with 532 nm in distilled water.

Perhaps, the morphology, size and structure of ablated products also depend on the laser ablation wavelength and energy. The higher power density (6.11 x 108 W/cm^2 – 1064 nm at 300 mJ) promotes the formation of smaller and agglomerated quasi-spherical Zn-$Zn(OH)_2$ nanoparticles and at low power density (4.02 x 108 W/cm^2 – 532 nm at 230 mJ) larger spherical ZnO nanoparticles.

It was reported that an increase in the laser energy lead to increase in the kinetic energy of ablated particles, in the plasma plume generated on the surface of target during ablation, to form smaller particles (Solati, Dejam, & Dorranian, 2014). Also, ZnO and ε-$Zn(OH)_2$ nanomaterials with different size and morphology were obtained by changing the laser ablation wavelength from 1064 nm to 532 nm (Lin et al., 2011).

4.2 XPS Analysis

Figure 6 shows the survey XPS spectra from the spherical ZnO nanoparticles prepared by ablation in 2-propanol using the 532 nm output laser beam (3.9 J/cm^2), indicating the presence Zn, O and adventitious C. No contaminants were detected on the sample surface. The high intensity showed by the C1s peak is due to the liquid media, which are composed of carbon other than from the environmental contamination when the samples were dried.

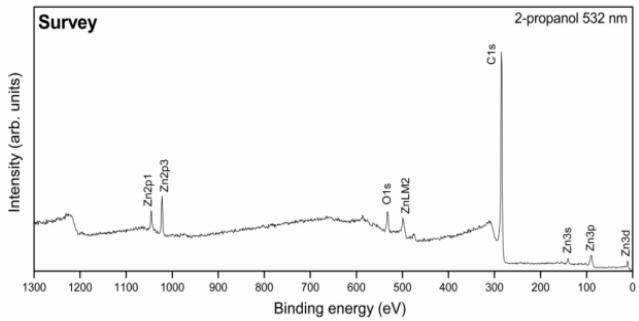

Figure 6 Survey analysis of the ZnO nanoparticles synthesis by ablation in 2-propanol (532 nm, 3.9 J/cm^2), made by XPS

Figure 7a shows the high resolution core level spectra Zn2p for the bulk zinc metal target and for the ZnO/$Zn(OH)_2$ nanomaterials obtained by ablation in distilled water and 2-propanol using the 532 and the 1064 nm output laser beam at 3.9 and 6.1 J/cm^2, respectively. Also, the O1s high resolution spectra of the as-synthesized nanomaterials by ablation are presented in Figure 7b.

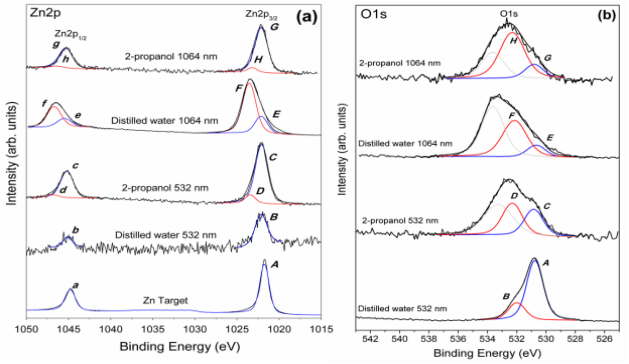

Figure 7 Zn2p and O1s high resolution core level spectra of the as-synthesized zinc nanomaterials by ablation in distilled wáter and 2-propanol using the 532 nm and 1064 nm output laser beam (3.9 and 6.1 J/cm2, respectively)

All the recorded binding energy data were corrected using C1s binding energy from adventitious carbon at 284.6 eV. Background (using Shirley method) and deconvolution of the spectra was done in the software of the XPS equipment (Avantage). All the recorded Zn2p and O1s binding energies are described in the Table 1 and Table 2 , respectively.

The reported binding energy of elemental Zn is 1021.8 eV for $Zn2p_{3/2}$ and the doublet separation (ΔE) is 22.97 eV (Moulder, Stickle, Sobol, & Bomben, 1992). The $Zn2p_{3/2}$ peaks located at the binding energy of 1022.1 and 1023.4 eV, are reported for Zn^{+2} in ZnO and $Zn(OH)_2$ phases, respectively.

The ZnO and $Zn(OH)_2$ nanoparticles are produced by ablation in distilled water and 2-propanol using the both laser wavelengths, and this is in agreement with the SAED pattern reported in . Figure 2 and Figure 3.

The O1s spectra were deconvoluted in 2-3 peaks as shown in Figure b, binding energies 530.8 eV and 532.0 eV correspond to O^{-2} in ZnO and in $Zn(OH)_2$ respectively.

Peak	Binding Energy (eV)	Compound
A	1021.8	Zn°
a	1044.8	Zn°
B	1022.1	ZnO
b	1045.1	ZnO
C	1022.1	ZnO
c	1045.2	ZnO
D	1023.4	$Zn(OH)_2$
d	1046.6	$Zn(OH)_2$
E	1022.1	ZnO
e	1045.3	ZnO
F	1023.5	$Zn(OH)_2$
f	1046.7	$Zn(OH)_2$
G	1022.1	ZnO
g	1045.3	ZnO
H	1023.2	$Zn(OH)_2$
h	1046.4	$Zn(OH)_2$

Table 1 Binding energies of the Zn2p core level spectra for the zinc nanomaterials synthesized by ablation in distilled water and 2-propanol, using the 532 nm and 1064 nm.

Peak	Binding Energy (eV)	Compound
A	530.8	ZnO
B	532.0	$Zn(OH)_2$
C	530.8	ZnO
D	532.3	$Zn(OH)_2$
E	530.7	ZnO
F	532.1	$Zn(OH)_2$
G	530.8	ZnO
H	532.3	$Zn(OH)_2$

Table 2 Binding energies of the O1s core level spectra for the zinc nanomaterials synthesized by ablation in distilled water and 2-propanol, using the 532 nm and 1064 nm

Hilon Hu et al. (Hu et al., 2011) reported the binding energy at 530.6 eV which was attributed to O^{2-} ions in wurtzite structure of hexagonal Zn^{2+} ion array. Also, they reported a peak at the binding energy of 531.2 eV and it was associated with O^{2-} ions in the oxygen-deficient regions within the matrix of ZnO. Fazio et al. (Fazio, Patanè, D'Urso, Compagnini, & Neri, 2012) reported XPS spectrum for a ZnO film on a silicon substrate obtained by spraying a colloidal solution of ZnO NPs prepared at two laser energies (20 and 150 mJ) of the second harmonic (532 nm) of a Nd:YAG laser operating at 10 Hz repetition rate with a pulse with of 5 ns.

ISSN-On line: 1390-9959

They reported the core line $Zn2p_{3/2}$ at 1021.8 eV for zinc in ZnO. The O1s structures for the two energies showed the presence of two distinct components at 530.3 eV (O^{2-} on normal wurtzite structure of ZnO single crystal) and 531.9 eV (O-H bonds). XPS spectral analysis confirmed that the ablation in both liquid mediums resulted in ZnO and $Zn(OH)_2$ phases.

4.3 UV-Visible Spectroscopy analysis

The different optical behavior of the samples is identified by the change in the slope of their optical absorbance in the visible region. The optical band gap is evaluated by extrapolating the Tauc plot for direct band gap materials. The influence of nanocrystal size on the electronic structure of semiconducting material is represented by the band gap increasing with decreasing of the particle size, which is attributed to the so-called quantum confinement effect (Dorranian & Eskandari, 2015; Kuncser & Miu, 2014; YU & Cardona, 2010). The optical absorbance spectra and the estimated optical band gap for the colloids prepared by ablation in distilled water and 2-propanol using the 532 nm and 1064 nm output laser beam are shown in Figure 8

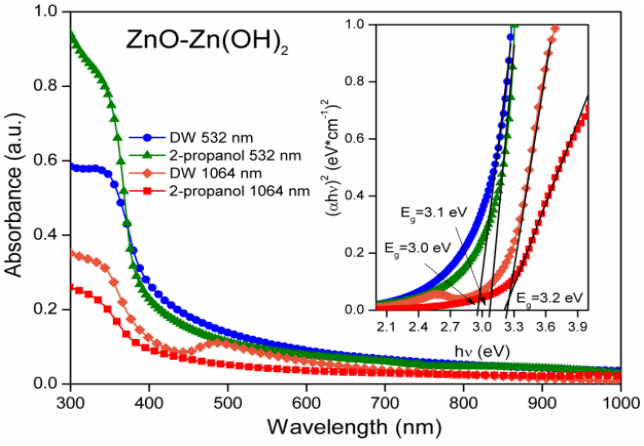

Figure 8 Absorption spectra and optical band gap (inset) of the Zn nanomaterials obtained by ablation in distilled water and 2-propanol (532 nm – 3.9 J/cm^2 and 1064 nm – 6.1 J/cm^2)

All the absorption edges and band gap energies are included in Table 3. There is a change in the optical band gap value to higher energies when the ablation is done with the 1064 nm output laser beam. By ablation in distilled water, smaller nanoparticles are synthesized and well dispersed spherical nanoparticles are prepared by ablation in 2-propanol, as shown in Figure 3

However, these optical band gaps are lower than the reported value for ZnO bulk semiconductor (3.3 eV) (Rodnyi & Khodyuk, 2011), and represent a red shift in the absorption spectra, which can be due to the presence of a broad size distribution of ZnO nanoparticles, or by the observed agglomeration (Kumar, Venkateswarlu, Rao, & Rao, 2013). An absorption edge at 380 nm and a broad absorption edge from 400 to 600 nm have been observed for ZnO nanoparticles prepared by PLALM of Zn metal target in distilled water and SDS, respectively. The absorption edges were indicative of the presence of a broad size distribution or relatively severe aggregation of the as-prepared ZnO nanoparticles (Hu et al., 2011).

5. Conclusions

ZnO and $Zn(OH)_2$ nanomaterials having different morphologies were synthesized by PLALM, changing the liquid medium and the laser ablation wavelength (532 nm, 1064 nm). The morphology, size, size distribution, crystalline structure and elemental composition of the zinc nanomaterials were analyzed using TEM, SAED and EDX. The elemental composition and chemical states of all the as-synthesized ZnO and $Zn(OH)_2$ nanomaterials were confirmed by XPS analysis. It was synthesized ZnO spherical nanoparticles (31 ± 13 nm) by ablation in distilled water using 532 nm, however, by changing the laser ablation wavelength to 1064 nm, more agglomerated and smaller $Zn(OH)_2$ nanoparticles (10 ± 5 nm) were obtained. Their size was dependant of the optical and chemical liquid medium properties and the laser wavelength used.

ISSN-On line: 1390-9959

6. Acknowledgments

The author is thankful to SEP- CONACYT – Mexico (Project 106955), CONACYT-Project 121124 and CEMIE-SOL, CONACYT – Mexico (Project 35) for the financial assistance in this work at the UANL. Grisel García Guillén is grateful to CONACYT-Mexico for providing a doctoral research fellowship.

7. References

Amendola, V., & Meneghetti, M. (2009). Laser ablation synthesis in solution and size manipulation of noble metal nanoparticles. [Research Support, Non-U.S. Gov't]. *Phys Chem Chem Phys, 11*(20), 3805-3821. doi: 10.1039/b900654k

Dev, A., Kar, S., Chakrabarti, S., & Chaudhuri, S. (2006). Optical and field emission properties of ZnO nanorod arrays synthesized on zinc foils by the solvothermal route. *Nanotechnology, 17*(5), 1533.

Djurisic, A. B., & Leung, Y. H. (2006). Optical properties of ZnO nanostructures. [Research Support, Non-U.S. Gov'tReview]. *Small, 2*(8-9), 944-961. doi: 10.1002/smll.200600134

Dorranian, D., & Eskandari, A. F. (2015). Effect of Laser Fluence on the Characteristics of ZnO Nanoparticles Produced by Laser Ablation in Acetone. *Molecular Crystals and Liquid Crystals, 607*(1), 1-12. doi: 10.1080/15421406.2014.927414

Dorranian, D., Solati, E., & Dejam, L. (2012). Photoluminescence of ZnO nanoparticles generated by laser ablation in deionized water. *Applied Physics A, 109*(2), 307-314. doi: 10.1007/s00339-012-7073-5

Fazio, E., Patanè, S., D'Urso, L., Compagnini, G., & Neri, F. (2012). Enhanced nonlinear optical response of linear carbon chain colloid mixed with silver nanoparticles. *Optics Communications, 285*(12), 2942-2946. doi: 10.1016/j.optcom.2012.02.039

Francis B. Dejene, A. G. A., Hendrik C. Swart, Reinhardt J. Botha, Kittesa Roro, Liza Coetsee, Mart M. Biggs. (2011). Optical properties of ZnO nanoparticles synthesized by varying the sodium hydroxide to zinc acetate molar ratios using a Sol-Gel process. *Central European Journal of Physics, 9*(5), 1321-1326. doi: 10.2478/s11534-011-0050-3

Gorla, C. R., Emanetoglu, N. W., Liang, S., Mayo, W. E., Lu, Y., Wraback, M., & Shen, H. (1999). Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on (01$\bar{1}$2) sapphire by metalorganic chemical vapor deposition. *Journal of Applied Physics, 85*(5), 2595-2602. doi: doi:http://dx.doi.org/10.1063/1.369577

Haase, M., Weller, H., & Henglein, A. (1988). Photochemistry and radiation chemistry of colloidal semiconductors. 23. Electron storage on zinc oxide particles and size quantization. *The Journal of Physical Chemistry, 92*(2), 482-487. doi: 10.1021/j100313a047

Hu, X., Gong, H., Wang, Y., Chen, Q., Zhang, J., Zheng, S., . . . Cao, B. (2012). Laser-induced reshaping of particles aiming at energy-saving applications. [10.1039/C2JM32041J]. *Journal of Materials Chemistry, 22*(31), 15947-15952. doi: 10.1039/c2jm32041j

Hu, X., Gong, H., Xu, H., Wei, H., Cao, B., Liu, G., . . . Cai, W. (2011). Influences of Target and Liquid Media on Morphologies and Optical Properties of ZnO Nanoparticles Prepared by Laser Ablation in Solution. *Journal of the American Ceramic Society, 94*(12), 4305-4309. doi: 10.1111/j.1551-2916.2011.04643.x

ISSN-On line: 1390-9959

Itina, T. E. (2011). On Nanoparticle Formation by Laser Ablation in Liquids. *The Journal of Physical Chemistry C, 115*(12), 5044-5048. doi: 10.1021/jp1090944

Kumar, S., Venkateswarlu, P., Rao, V., & Rao, G. (2013). Synthesis, characterization and optical properties of zinc oxide nanoparticles. *International Nano Letters, 3*(1), 1-6. doi: 10.1186/2228-5326-3-30

Kuncser, V., & Miu, L. (2014). *Size Effects in Nanostructures: Basics and Applications*: Springer Berlin Heidelberg.

Liang, C., Tian, Z., Tsuruoka, T., Cai, W., & Koshizaki, N. (2011). Blue and green luminescence from layered zinc hydroxide/dodecyl sulfate hybrid nanosheets. *Journal of Photochemistry and Photobiology A: Chemistry, 224*(1), 110-115. doi: http://dx.doi.org/10.1016/j.jphotochem.2011.09.013

Lin, B. C., Shen, P., & Chen, S. Y. (2011). ZnO and ε-Zn(OH)2Composite Nanoparticles by Pulsed Laser Ablation on Zn in Water. *The Journal of Physical Chemistry C, 115*(12), 5003-5010. doi: 10.1021/jp107140r

Moulder, J. F., Stickle, W. F., Sobol, P. E., & Bomben, K. D. (1992). *Handbook of X-ray Photoelectron Spectroscopy*. USA: Perkin-Elmer Corp.

Pan, Z. W., Dai, Z. R., & Wang, Z. L. (2001). Nanobelts of Semiconducting Oxides. *Science, 291*(5510), 1947-1949. doi: 10.1126/science.1058120

Rao, S. V., Podagatlapalli, G. K., & Hamad, S. (2014). Ultrafast Laser Ablation in Liquids for Nanomaterials and Applications. *Journal of Nanoscience and Nanotechnology, 14*(2), 1364-1388. doi: 10.1166/jnn.2014.9138

Rodnyi, P. A., & Khodyuk, I. V. (2011). Optical and luminescence properties of zinc oxide (Review). *Optics and Spectroscopy, 111*(5), 776-785. doi: 10.1134/s0030400x11120216

Shoutarou, T., Yuhei, H., Atsushi, N., Takeharu, T., Masamichi, I., Osamu, O., & Hiroyuki, W. (2010). Optical Properties of Laser-Irradiated ZnO Nanoparticles in 2-Propanol. *Japanese Journal of Applied Physics, 49*(5R), 052602.

Singh, S. C., Swarnkar, R. K., & Gopal, R. (2010). Zn/ZnO core/shell nanoparticles synthesized by laser ablation in aqueous environment: Optical and structural characterizations. *Bulletin of Materials Science, 33*(1), 21-26. doi: 10.1007/s12034-010-0003-2

Solati, E., Dejam, L., & Dorranian, D. (2014). Effect of laser pulse energy and wavelength on the structure, morphology and optical properties of ZnO nanoparticles. *Optics & Laser Technology, 58*(0), 26-32. doi: http://dx.doi.org/10.1016/j.optlastec.2013.10.031

Song, J., Kulinich, S. A., Yan, J., Li, Z., He, J., Kan, C., & Zeng, H. (2013). Epitaxial ZnO Nanowire-on-Nanoplate Structures as Efficient and Transferable Field Emitters. *Advanced Materials, 25*(40), 5750-5755. doi: 10.1002/adma.201302293

Thareja, R. K., & Shukla, S. (2007). Synthesis and characterization of zinc oxide nanoparticles by laser ablation of zinc in liquid. *Applied Surface Science, 253*(22), 8889-8895. doi: http://dx.doi.org/10.1016/j.apsusc.2007.04.088

Wagener, P., Faramarzi, S., Schwenke, A., Rosenfeld, R., & Barcikowski, S. (2011). Photoluminescent zinc oxide polymer nanocomposites fabricated using picosecond laser ablation in an organic solvent. *Applied Surface Science, 257*(16), 7231-7237. doi: http://dx.doi.org/10.1016/j.apsusc.2011.03.097

ISSN-On line: 1390-9959

Wagener, P., Schwenke, A., Chichkov, B. N., & Barcikowski, S. (2010). Pulsed Laser Ablation of Zinc in Tetrahydrofuran: Bypassing the Cavitation Bubble. *The Journal of Physical Chemistry C, 114*(17), 7618-7625. doi: 10.1021/jp911243a

Yang, S., Kiraly, B., Wang, W. Y., Shang, S., Cao, B., Zeng, H., . . . Huang, T. J. (2012). Fabrication and Characterization of Beaded SiC Quantum Rings with Anomalous Red Spectral Shift. *Advanced Materials, 24*(41), 5598-5603. doi: 10.1002/adma.201202286

YU, P., & Cardona, M. (2010). *Fundamentals of Semiconductors: Physics and Materials Properties*: Springer.

Zeng, H., Cai, W., Li, Y., Hu, J., & Liu, P. (2005). Composition/Structural Evolution and Optical Properties of ZnO/Zn Nanoparticles by Laser Ablation in Liquid Media. *The Journal of Physical Chemistry B, 109*(39), 18260-18266. doi: 10.1021/jp052258n

Zeng, H., Du, X.-W., Singh, S. C., Kulinich, S. A., Yang, S., He, J., & Cai, W. (2012). Nanomaterials via Laser Ablation/Irradiation in Liquid: A Review. *Advanced Functional Materials, 22*(7), 1333-1353. doi: 10.1002/adfm.201102295

Zeng, H., Duan, G., Li, Y., Yang, S., Xu, X., & Cai, W. (2010). Blue Luminescence of ZnO Nanoparticles Based on Non-Equilibrium Processes: Defect Origins and Emission Controls. *Advanced Functional Materials, 20*(4), 561-572. doi: 10.1002/adfm.200901884

Zeng, H., Li, Z., Cai, W., Cao, B., Liu, P., & Yang, S. (2007). Microstructure Control of Zn/ZnO Core/Shell Nanoparticles and Their Temperature-Dependent Blue Emissions. *The Journal of Physical Chemistry B, 111*(51), 14311-14317. doi: 10.1021/jp0770413

Zhao, C., Huang, Y., & Abiade, J. T. (2012). Ferromagnetic ZnO nanoparticles prepared by pulsed laser deposition in liquid. *Materials Letters, 85*, 164-167. doi: http://dx.doi.org/10.1016/j.matlet.2012.06.088

ISSN-On line: 1390-9959