Study the Effect of Molarity on the Synthesis Nanoparticles by Liquid-Phase Laser Ablation Technique

Suha I. Al-Nassar

Abstract— ***This work was focused on the studying the effect of molarity on the producing ZnO nanoparticles by Liquid –Phase Pulsed Laser Ablation (LP-PLA) of Zn metal plate in the aqueous environment of cetyl trimethyl ammonium bromide (CTAB) using femtosecond laser (Ti-Sapharie has wavelength= 800 nm, rep. rate= 1K Hz, Pulse duration =130 fs and laser energy pulse 0.5 mJ. The effect of molarity on the optical and structure of ZnO was studied is characterized by UV-visible absorption. UV-visible absorption spectrum has three peaks at 220, 210 ,204 nm for different values of molarity (10^{-2}, 10^{-3} and 10^{-4}) respectively, our results show that UV–visible spectra show a blue shift with decrease the molarity of CTAB solution because this leads to decrease the concentration of ZnO NPs and decreases the the aggregate of surfactant molecules dispersed in liquid collide ,and blue shift indicated to get smaller size of nanoparticles. The blue shift in the absorption edge indicates the quantum confinement property of nanoparticles. Also FTIR transmittance spectra of ZnO_2 nanoparticles prepared in these states show a characteristic ZnO absorption at 435–455cm^{-1}.***

Keywords—***Ablation time, CTAB solution, pulsed laser ablation technique, Zinc oxide nanoparticles.***

I. INTRODUCTION

The properties of nanoparticles show great differences in electric, optical, magnetic and chemical properties from the bulk material of which they are made [1].

There are many physical and chemical routes to produce nanomaterial .[2].

Pulsed Laser Ablation in liquid environments (PLAL) represents one of the most important techniques for preparing various kinds of nanomaterial. This technique has been proven an effective and simple technique for preparing metal, metal oxide, metal peroxide nanoparticles and it has many advantages compared to the other conventional physical and chemical methods are as follows: (1) inexpensive equipment for controlling the ablation atmosphere, (2) simplicity of the procedure, and (3) the minimum amount chemical species required for synthesis compared to the conventional chemical process [1-3].

Generating NPs through PLAL technique passes through three fundamental steps. Firstly plasma generates due to extreme heating during the interaction of laser with matter.

Secondly the ultrasonic adiabatic plasma expand leads to quick cooling of the plume region and hence to the formation of nanoparticles clusters. Finally after plasma extinguishing the formed nanoparticles clusters encounter and interact with the solvent and surfactant molecules in the surrounding solution.

Manuscript Received on May 2015.

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Those processes involve the nucleation and phase transition of nanocrystals [3]. During these steps, nucleation of the target atoms takes place and, as a result, the fine nuclei stick together, in other words the mechanisms involved in the nucleation and phase transition of nanocrystals [4], [5].

Due to their size and shape dependent properties, nanodimensional semiconductor materials have shown their great interest in optoelectronics, electronics, sensing, energy storing and harvesting applications.

The concept of producing oxide using laser irradiation of metal targets in water was demonstrated in 1987 where iron and tantalum oxides were formed on target surfaces in water using a Q-switched ruby pulsed laser by using a third harmonic of a pulsed Nd:YAG laser PLAL of Ti in water and SDS solution [6]. Sasaki et al [7] have synthesized TiO2 in both deionized water and sodium dodecyl sulfate (SDS) solutions and they have explained crystallinity of the nanoparticles strongly depended on the SDS concentration in the solution. The metal oxide nanoparticles have many applications in nonlinear optics, optoelectronics, biomedical engineering, electro-optical devices and chemical catalysts [8].

Zinc oxide is promising semiconductor material with unique properties of UV emission, optical transparency, electric conductivity, and piezo electricity due to a wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature even compared with other semiconducting nanoparticles [2]. Its potential for advanced applications in lasers, as bio-imaging agent, in biosensors and as drug delivery vehicles, in ointments, coatings, also it is transparent to most of the solar spectrum; therefore, widely used as window material in solar cells, optical waveguides, light modulators and optical sensors [8].

Zinc oxide nanoparticles can be synthesized in a myriad of ways, including physical vapor deposition, an organometallic precursor method, via precipitation solvothermal and hydrothermal methods, and sol–gel methods such as sol–gel combustion However pulsed laser ablation of solids in solution (PLAL) has been shown to be an effective, flexible and efficient technique for preparing ZnO nanoparticles with high purity and without surface contamination by residual anions and reducing agents. Many reports in the literature show that significant effort is put into adapting this technique in such a way that particle size and shape can efficiently and accurately be controlled. Such as li. Fojtik and Henglein (1993) and Cotton et al (1993, 1996) have used several liquids as ablation media to produce colloidal solution of nanoparticles [2], [9]. This paper was devoted on synthesis ZnO- NPs and studies the effect of molarity in controlling the

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size and stability of generated ZnO NPs in CTAB solution. ZnO-NPs were characterized by FTIR, UV–vis spectroscopy, UV–visible in order to evaluate absorption spectra, particle size and size distribution, and overall composite structure.

II. Experimental Work

Zinc nanoparticles were produced by pulsed laser ablation of a piece of zinc metal (fello Co., Inc.; 99.9%) in an aqueous solution of CTAB using distilled water as a solvent, A zinc metal plate was placed on the bottom of an open glass vessel filled with 10 mL of aqueous solution.

Fig. 1 shows a schematic diagram of the laser based set-up for synthesis of nanoparticles using a pulsed Ti/Sapphire laser beam (Quadronix IntenC laser) .This laser operates at 1 kHz repetition rate with a pulse width of ≤130 fs at 2.5 mJ/pulse maximum laser beam output, it is focused via a 100 mm focal length focusing lens to a minimum spot size at Kocaeli University Laser Technologies Research and Application Center (LATARUM)) was vertically irradiated onto a Zn plate placed in the aqueous solution. The collimated beam at 800 nm is tightly focused on the target sample using a convex lens in order to get sufficient laser fluence for the ablation.

Cetyl trimethyl ammonium bromide (CTAB) solution was added to the solution to control the size and/or prevent the aggregation of the products. The ablation was performed at different values of molarity (10-2, 10-3 and 10-4) to study the effect of the molarity on the properties of the prepared nanoparticles.

After using different values of concentration a grey colloidal solution of oxide-based nanomaterials was obtained. A magnetic stirrer rotator was placed in the solution rotates at 600 rpm to ensure uniform irradiation on target and the movement of water that can enhance ablated particle diffusion also to disperse the produced NPs. Laser power was measured via a power meter type Newport 841-PE, the measurement was obtained at two locations very near to the final stage of the laser apparatus and before the focusing lens to evaluate the losses of the power in the beam delivery unit. Before starting the experiment the zinc target was cleaned by ultrasonic cleaning device type EMAG 50 HC then wiped with acetone and ethanol solvents.

The prepared ZnO-NPs were initially characterized using a number of tests were done to characterize the produced zinc oxide NPs, UV-visible extinction spectrum of the colloidal solutions was recorded using a spectrophotometer type spectrophotometer type Varian Cary-50 UV-Visible with 1 cm optical path cell in order to study the optical absorption/transmission properties of nanoparticle-dispersed suspensions, NPs Size, Other analytical techniques such as (FTIR) spectroscopy (The PerkinElmer Spectrum 100 Series FT-IR spectrometer) are also used to study the adsorption of organic species on the ZnO nanoparticles. FTIR spectra were measured at room temperature with the spectrometer using the KBr Pellet technique [10]. Samples were lyophilized, gently mixed with 300 mg of KBr powder and compressed into discs at a pressure of 40 MPa for 5min, range of 400–4000 cm−1 to know the chemical bonding of the produced nanoparticles.

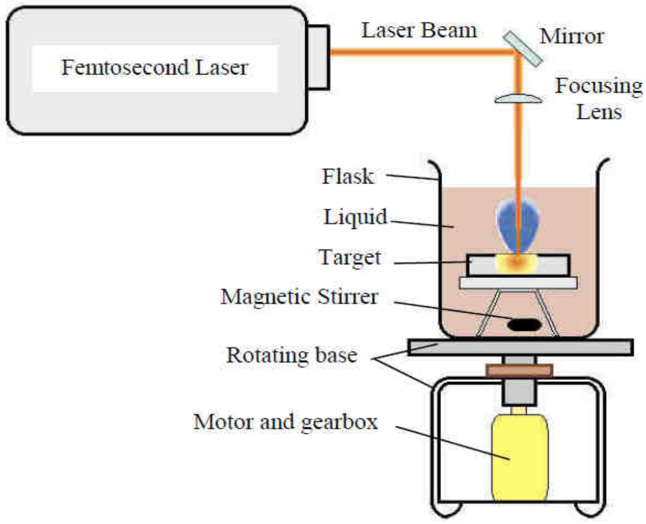

Fig. 1 The set up experiment of femtosecond laser ablation

III. Results and Discussion

In the experiments of this research work, laser ablation of the zinc target in CTAB solution at different molarity (concentration) was investigated, this process accompanied by the production of a plasma plume, visible to the eye, near the target surface also the change of color of ZnO colloidal solution to grey wish color indicates that nanosized colloidal particles have produced. The Shape and the size distributions of ZnO nanoparticles in different concentration of ablation were characterized by many inspections such as (UV-visible and FTIR). The Effect of molarity of aqueous solution on UV–visible absorption peak are presented in Table I according to this table a blue shift in the presence of CTAB with decrease the molarity and blue shift indicated to get smaller size of nanoparticles .

Fig. 2 displays the absorption spectra of ZnO produced in three values of molarity (10-2, 10-3, 10-4). It was obvious that colors of liquids were changed differently within the process. During the laser ablation in (samples S1), prepared colloid became opaque slowly, and finally, it tended to grey color after 5 min of ablation, after that the samples S2 became grey faster than the first sample, in sample S3 , it tended to milky color after ablation for 10 min.

TABLE I
EFFECT OF DIFFERENT MOLARITY ON UV–VISIBLE ABSORPTION PEAK (*_λ= 800 nm, E= 0,5 mJ/pulse)*

Sample code	Molarity of solution	UV-vis.absorption peak wave length(nm)
S1	10^{-2}	220
S2	10^{-3}	210
S3	10^{-4}	204

On the other hand, fine bobbles were formed in front of target S3 after first 15 min of ablation.

These bobbles apparently prohibited the laser energy to be absorbed by target, which could easily be realized by extremely diminished noises of impacts. The absorption bands centered at(220, 210, 204 nm) about peaks at for molarity (10^{-2}, 10^{-3} and 10^{-4}) respectively.

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According to the fig. 2 the Plasmon band of the colloidal ZnO is shifted to blue shift (smaller wavelength) with decreases the molarity (concentration) , These observations reflect the formation of small ZnO particles, but by increasing the concentration , the optical absorption reveals a broad band with a long tail toward the longer wavelengths, indicating the formation of inhomogeneous sizes, because when surfactant concentration is small (<CMC Critical Micelles Concentration), the aqueous oxidation effect will be dominant. At lower laser irradiance and smaller amount of surfactant, this leads to vapor small number of atoms which gets aqueous oxidized and form ZnO clusters of 1–20 nm diameter. In contrast at large laser irradiance or/and higher surfactant concentration large number of atoms get vaporized, which form larger metal clusters of 100 nm diameters At higher surfactant concentration and strong capping on the surface of the nanoparticles is achieved by CTAB molecules, which prevents it for aqueous oxidation and synthesis of pure zinc nanoparticles is done.

In other words when surfactant concentration is low CMC, surfaces of the nanoparticles with large diameter are weakly capped by CTAB which gets oxidized to form Zn core of large diameter with small thickness of ZnO shell. It means that mostly large sized particles synthesized by laser ablation in near CMC of surfactant have Zn core and ZnO shell, while those of small sized ones are completely of zinc oxide as in the case of present investigation [11].

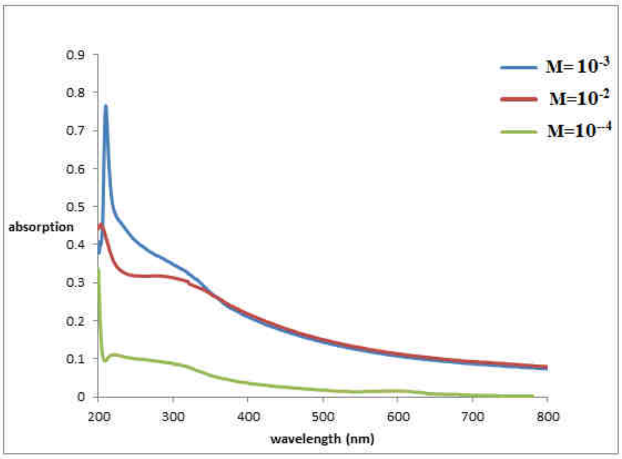

Fig. 2 UV–visible absorption spectra of ZnO nanoparticles prepared in different values of CTAB molarity (λ 800 nm, E = 0.5 mJ/pulse,)

Also Fourier transform infrared (FTIR) spectra were measured at room temperature with an FTIR spectrometer using the KBr pellet technique. FTIR measurements are essential to confirm the formation of crystalline ZnO nanocrystals and to identify any adsorbed species onto the surface of nanoparticles.

Samples were lyophilized gently mixed with 300mgof KBr powder and compressed into discs at a force of 13kN for 5min using a manual tablet presser. FTIR spectrum was recorded in the spectral range of 400–4000cm^{-1}.

The FTIR was found to be very useful for understanding bonding between Zn-O atoms or molecules. In Fig. 3 the spectra show a characteristic ZnO absorption at 435–455cm^{-1} for the nanoparticles produced in the absence and presence of surfactants. There are also other bands at 1040–1070cm^{-1} present in the spectra which may arise from the O–O bands, the absorption peaks at 3408 and 2924 cm^{-1} are attributed to O–H stretching vibration from ZnOH species and C–H stretching vibration, respectively. The free O–H stretching bond at 3408 cm^{-1} arises due to reaction of ZnO nanoparticles and hydroxyl group these results are consistent with that reported in the literature [2], [9].

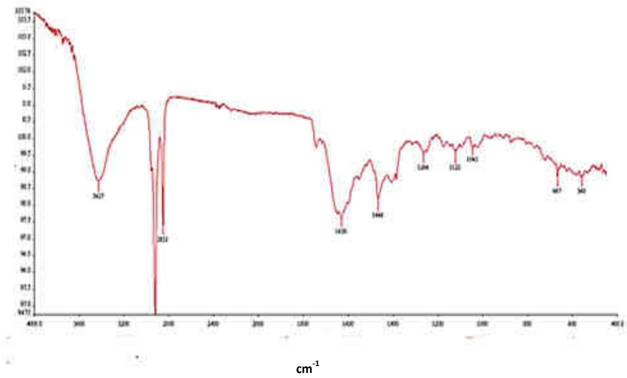

Fig. 3 FTIR spectra of ZnO nanoparticles prepared in CTAB Media (λ = 800 nm, E = 0,5 mJ/pulse)

IV. Conclusion

In summary, this research work has successfully produced ZnO nanoparticles by pulsed laser ablation of Zinc target in different values of CTAB molarity, the study of effect molarity was carried out for 10^{-2}, 10^{-3} and 10^{-4} in constant conditions (wavelength= 800 nm, rep. rate= 1K Hz, Pulse duration =130 fs and laser energy pulse 0.5 mJ,). UV-visible absorption spectrum has different peaks at 220, 210, 204 nm for different molarity (10^{-2}, 10^{-3} and 10^{-4}) respectively, our results show that UV–vis spectra show a blue shift in the presence of CTAB with decrease the concentration and blue shift indicated to get smaller size of nanoparticles It was seen that the decrease of concentration ZnO NPs leads to decreases the aggregate of surfactant molecules dispersed in liquid collide ,and blue shift indicated to get smaller size of nanoparticles. The blue shift in the absorption edge indicates the quantum confinement property of nanoparticles.

Acknowledgment

This work was supported by Laser Technologies Research and Application Center (LATARUM) at Kocaeli University in Turkey) and the Ministry of Higher Education of Iraq.

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