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ABSTRACT: *In the recent years, laser ablation in liquid has become an increasingly important technique for the fabrication of NPs. this paper reports our recent studies on the generation of ZnO NPs by ablation of metal targets in aqueous environments using Q-switch Nd-YAG laser (λ=532nm) immersed in NaOH (0.1M). The Surface topography studied by atomic force microscopy revealed wider size distributions, with particle sizes (80.76 nm to 102.54nm)and shape were measured by using SEM shows spherical shape while the composing of the prepared nanoparticle were determined by X-ray, UV-Visible spectroscopy has been employed for the optical properties, the UV-VIS spectrum of the produced solution shows red shifted in the peak position with the laser ablation energy. The produced collide was a good stable.*

KEYWORDS: *ZnO; Laser ablation of metals in liquids; Nanoparticles; Plasmon resonance.*

INTRODUCTION

The properties and behavior of material at the nano-scale or level vary greatly when compared to micro levels. The properties of nanoparticles show great differences in electric, optical, magnetic and chemical properties from the bulk material of which they are made[1] These properties are completely related to the size of particles which are not seen in the bulk state[2,3] Zinc oxide (ZnO) is a wide band gap semiconductor with an energy gap of 3.37 eV at room temperature. It has been used considerably for its catalytic, electrical, optoelectronic, and photochemical properties [6-9]. ZnO nanostructures have a great advantage to apply to a catalytic reaction process due to their large surface area and high catalytic activity [10].

Laser ablation of a solid target in liquids is a simple and reliable method for the generation of NanoParticles (NPs) of almost any metals and semiconductors. Generating of NPS through PLAL technique passes through three fundamental steps. Firstly plasma generates due to extreme heating during the interaction of laser with mater. Secondly, the ultrasonic adiabatic plasma expands leads to quick cooling of the plume. Finally, after plasma extinguishing the formed nanoparticles clusters encounter and interact with the solvent and surfactant molecules in the surrounding solution .those processes involve the nucleation and phase transition of nanocrystals [9,10,12,13].

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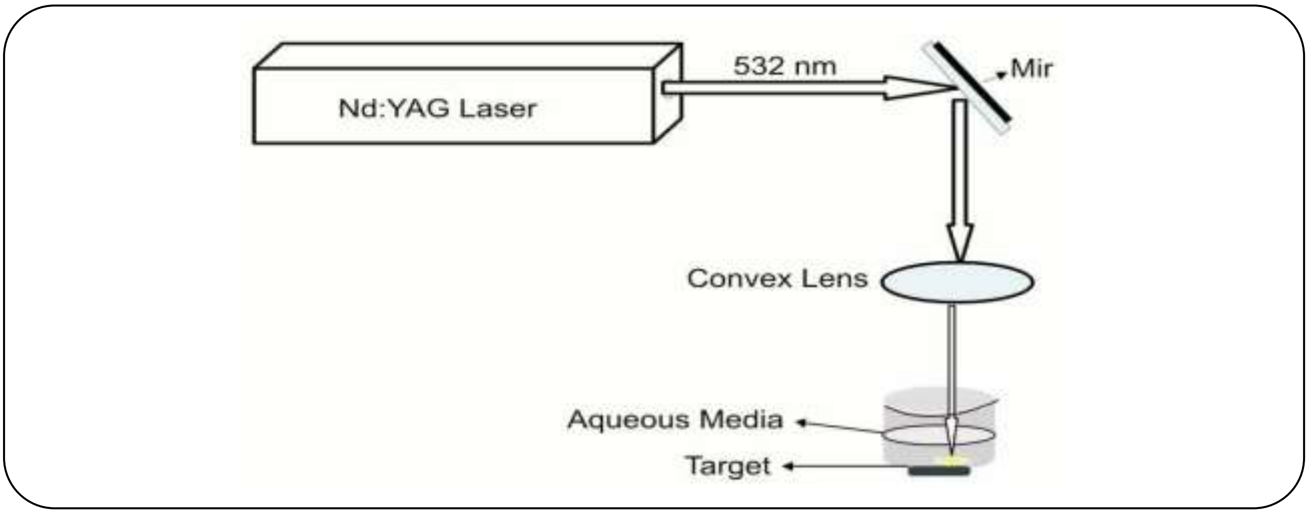

Fig. 1: Experimental arrangement.

The aim of the work is to study the effects of the NaOH solution on the composed and the stability of prepared NPS since NaOH represents the base medium for many chemical reactions occur during nanoparticles formation and also the effects of laser energy on the concentration of the synthesis NPS.

EXPERIMENTAL SECTION

Fig. 1 shows the schematic diagram of PLAL experimental setup for synthesis colloidal solution of ZnO NPs. The laser used in this work is a nanosecond Q-switched Nd-YAG LASER. Its operates at 532nm wavelength, 50 pulses number ,6Hz pulsed repetition rate and <10ns pulse duration at energy of (80, 140, 200, 26, 3209) mL ,the laser beam is focused on the target surface with diameter of 1mm Zinc target(purity 99.99%) was placed at the bottom of the quartz cell and immersed at 8mm depth in the solution of NaOH (0.1M).

The absorption spectra of the colloidal solutions was measured using UV-Visible, NPs size and surface morphology were examined using AFM, while the shape of NPs examined by SEM.

RESULTS AND DISCUSSION

Laser synthesis of ZnO NPs using different fluences. Samples were characterized by absorption spectroscopy, SEM, and XRD. The control of Nano collide composition and structure during Laser ablation in liquids is vital for accomplishing metastable stages, and for planning multifunctional nanoparticles with ideal sizes also, arrangements for particular applications in Nano medicine magneto-plasmonics, detecting or catalysis.

The practical set up of Laser ablation in liquids is moderately basic and permits the examination of the pretended by the concoction condition on the structure and creation of NPs by keeping up the various combination parameters unaltered.

The comparison of literature results for different target materials is not straightforward, because physical and chemical effects are mixed and experimental parameters (for instance the use of water or of organic solvents) are not homogeneous. However, in most cases, it is possible to find analogies, especially when target materials with similar chemical-physical properties are ablated.

The solvent strongly influences the composition and the structure of nanomaterial obtained by laser ablation in liquids.In our work used NaOH solution in ablation of Zn target that produced ZnO Nano collides. In most of the reported synthetic methods, nanoparticles are synthesized in the presence of a stabilizer such as surfactants or ionic polymers. However, these stabilizers cannot be easily removed from the silver colloids and this would consequently influence the physical and chemical properties of the synthesized nanoparticles.

Fig. 2 displays the absorption spectra of ZnO nanoparticle produced in NaOH (0.1M) medium. The UV-Visible absorption spectrum of the synthesized colloidal solution of nanoparticles shows the flat SPR peak present in the UV-Visible absorption spectrum indicates the formation of Tinn oxide NPs, which is confirmed

Table 1: Shows Laser Energy Vs. Fluence of laser beam.

Laser Energy (mJ)	Fluence(J/cm^2)
80	2.55
140	4.46
200	6.37
260	8.28
320	10.19

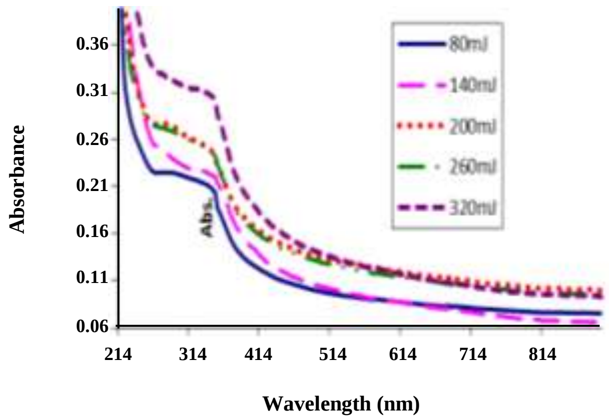

Fig. 2: Absorbance spectra of ZnO in NaOH (0.1M), λ=532nm, 50 pulses with different energy values.

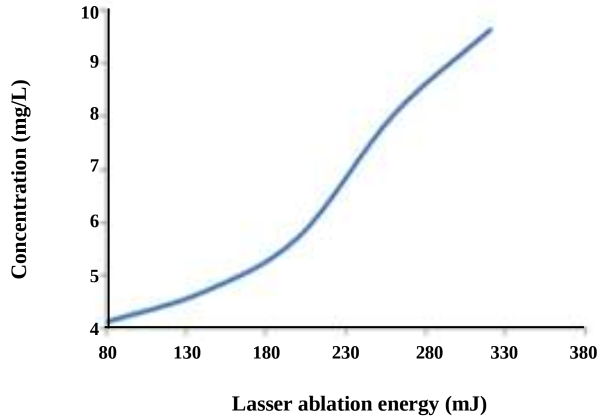

Fig. 3: The effects of laser ablation energy on the NPs concentration.

by XRD analysis also. Absorption peak shows a red shift in the position of absorption peak, also absorbance shows an increase in the Plasmon peak with increasing the laser energy, indicating to the increase in the concentration of NPs[11], as shown in Fig. 3. Also, the Surface Plasmon Resonance (SPR) affected by both the NPs size and by the solution. The LSPR peak wavelength of NPs is a function of surrounding refractive index and generally redshifts with an increase in refractive index. Media of high refractive indices are effectively more polarisable and thus couple with the surface plasmon electrons more readily and the energy required to collectively excite the electrons are decreased. This results in the reduction of the surface plasmon resonance energy and forms the basis of LSPR based refractive index sensing.

Increasing the laser energy or (Fluence variation between 2.55 – 10.19 J/cm^2) as in Table 1. Also increases the the local concentration of NPs in the proximity of the crater, because of the time for NPs diffusion away from the ablated region is reduced. This effect can favor the aggregation and the coalescence of NPs, but also the scattering of incoming laser pulses and the consequent decrease in the ablation yield. [14,15]. The stability of the colloidal was about (6 days) after preparation. The stability of the colloidal dispersion depend on the electrostatic attraction of their constituents, where there is a competition between aggregation and coalescences. Another important effect is that when the fluences are increased, the volumetric (grain size) distribution of the ablation products will be broad, this means that different grain sizes will be generated, thus increasing the chance of cluster. Recent studies using a two-temperature hydrodynamic model reveal that additional melting and erosion of the target stem from reflection of the metastable liquid layer back towards the surface due to the low compressibility of the liquid and expansion of the liquid–gas region immediately above the molten layer. One limitation of these simulations is that the influence of the collapse of the central cavitation bubble is not included or modeled, at least in the sense of the cavitation bubble observed by experimental studies [16,17].

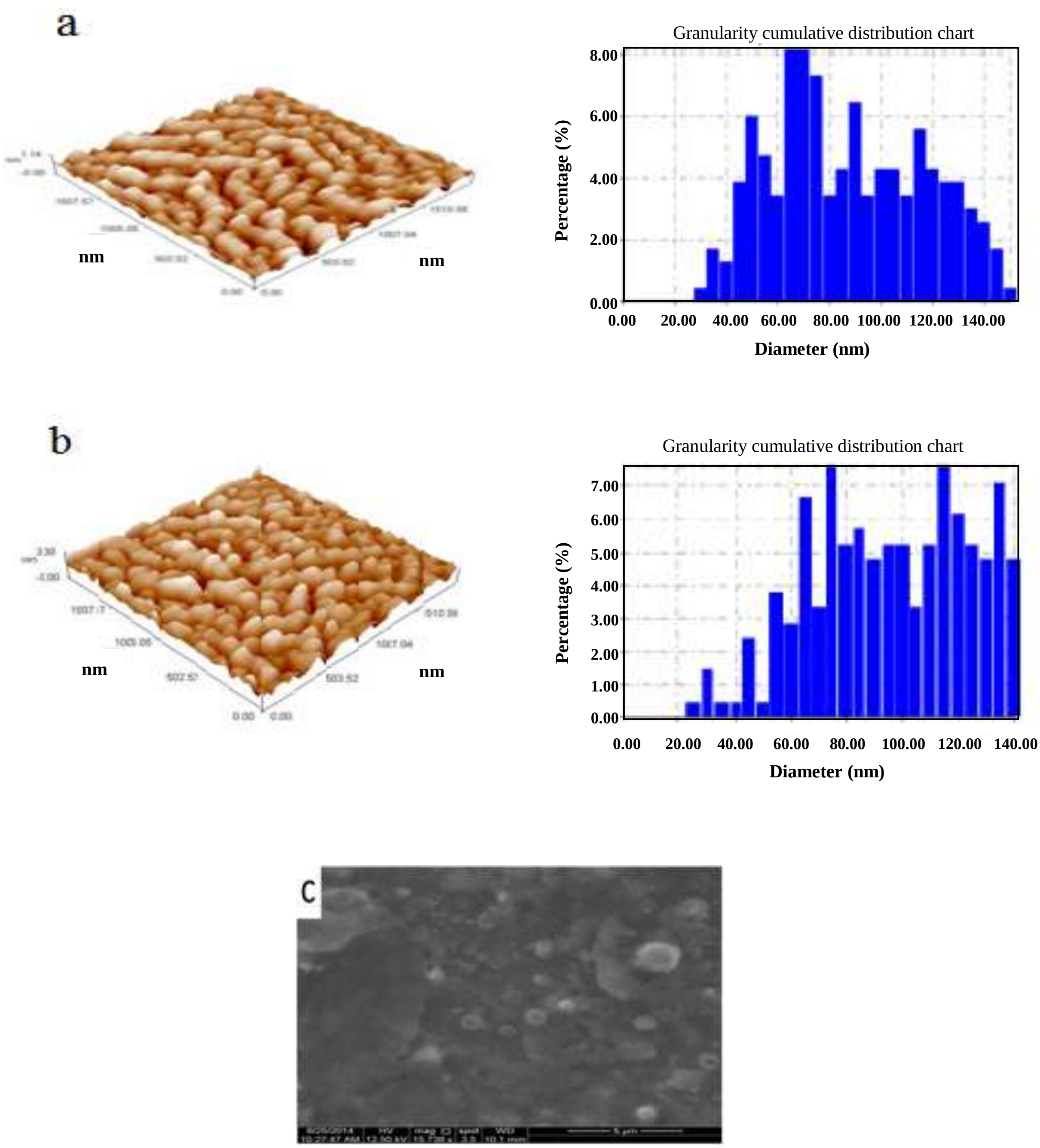

Fig. 4: AFM and SEM of ZnO nanoparticle in NaOH (A-at 80mJ, B-at 320mJ and C-SEM).

Fig. 4(a,b) shows AFM image of the ZnO nanoparticles obtained in NaOH aqueous solution, The diameters of the particles(grain size) were (80.76 nm) at 80mJ and(102.54nm) at 320mJ and this result shows as the energy of ablation increase the particle size increase, SEM measurements appeared that the formed particle is spherical in their shape Fig.3(C). According to X-ray diffraction measurement, the particle formed was ZnO as revealing in Fig. 5. The prepared collide was more stable for more than three months. These results were in agreement with other methods [18].

XRD pattern of the as synthesizes Nano powder dried at 60ºC is illustrated in Fig. 5. XRD pattern reveals intense and wide diffraction peaks at 2θ = 32.3º, 34.10º,

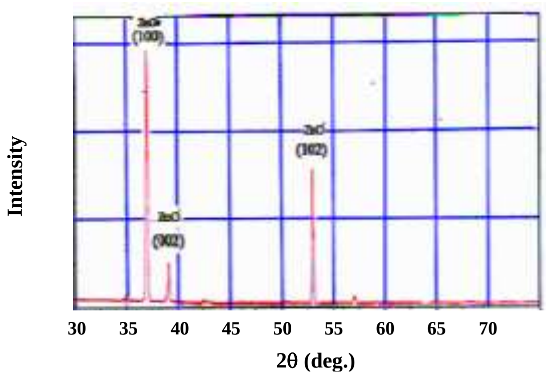

Fig. 5: X-ray diffraction pattern of ZnO NPs in NaOH(0.1M). λ=532nm.

and 48.10°. Out of these peaks, there are three less intense peaks at 2θ = 52.13º and 54.93º also observed. The peak at 2θ = 32.3º ° corresponds to the (100) plane of ZnO, 2θ = 34.10º corresponds to (002) plane of ZnO while the peak at 2θ =48.10. The crystallite sizes can be estimated using Scherrer's formula

$$D = K\lambda / \beta\cos\theta \qquad (1)$$

Where the constant *K* is taken to be 0.94, *λ* is the wavelength of X-ray used which is CuKα radiation (λ= 1.5406 Å), and β the full width at half maximum of the diffraction peak corresponding to 2θ. Using equation (1), the crystallite sizes found to be in the range of 35-40nm.

CONCLUSIONS

In summary, this research work has successfully produced spherical ZnO nanoparticles by using a simple method of nanosecond pulsed laser ablation in NaOH. No additives, such as solvents, surfactants or reducing agents, are needed in the procedure. Optical measurements of colloidal ZnO NPs exhibit single maximum optical extinction. Plasmon absorption of zinc nanoparticles shows that they are potential candidates for wide band gap (3.95 eV) semiconducting and ultra-violet lasing materials. They can also be used as good insulating material by a further reduction in size using ablation and fragmentation.

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