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PHOTOCHEMISTRY AND MAGNETOCHEMISTRY

# Influence of Laser Irradiation on the Optical Properties of Nano-Sized Powder of Metal Oxide[1]

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**Abstract**—ZnO Nano powders were prepared by co-precipitation method which includes post-oxidation and annealing in air. Influence of laser irradiation was carried out using 355 nm laser on the physical properties of ZnO nanoparticles. SEM studies reveal agglomeration of grains resulting into enlargement and deformation of the nanoparticles. XRD pattern exhibited decrease in FWHM which is a clear evidence of the increase in crystallite size due to laser irradiation. Optical properties showed decrease in the band gap of the laser irradiated Nano powders. The observed results indicated the UV laser irradiation increases the ZnO nanoparticles crystallinity that affects the optical properties of the ZnO.

*Keywords:* nanoparticles, laser irradiation, co-precipitation, post-oxidation.

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## 1. INTRODUCTION

Nanoparticles have wide range of applications in many fields of science and technology because of tremendous increase in the surface area to volume ratio [1–3]. Large surface area is an important factor in chemical reactions. In the nano scale materials, interaction on atomic scale dominates and exhibits quantum mechanical behavior as compared to bulk materials. Behavior of light interaction with materials also changes drastically as we go down to the nano size of the materials. This is due to decrease in the dimensions below the critical wavelength of light [4]. There are many methods for nanoparticle generation [5–8]. In the recent past, several preparation methods comprising ZnO quantum dots were used to develop nano size optical devices identified as nanophotonic devices [9, 10]. With the use of nanophotonic devices, one can reduce the device size away from the diffraction limit of light and attain unusual functionality unattainable by means of conventional photonic devices. Moreover, nanophotonic devices lessen power consumption and accomplish energy savings. In the literature, several researchers have demonstrated AND gate [11–13], NOT gate [14], nanoscale optical energy transfer devices [15], and nanoscale light-harvesting nanofountains [16] as nanophotonic devices. Numerous semiconductor materials which include CuCl [9, 11, 16], InAs [13, 14], and CdCe [15, 17], have been used for nanophotonic devices. Especially, ZnO is a promising material because of its large exciton binding energy and good optical properties at room temperature [18, 19]. Liu et al. reported Controlling the size of ZnO quantum dots using the dressed photon–phonon-assisted sol–gel method. Size distribution of ZnO QDs grown without light irradiation and with 325 nm laser irradiation has been studied [20]. In order to obtain high-performance nanophotonic devices, the size of ZnO nanoparticles must be tailored to reduce the size difference and resonate the discrete exciton energy level of nanoparticles.

We have synthesized the ZnO nanoparticles with co-precipitation technique and studied the effect of laser irradiation on the structural morphology at the wavelength of 355 nm from Nd: YAG laser system.

## 2. SYNTHESIS AND IRRADIATION OF ZnO NANOPARTICLES

ZnO nanoparticles were prepared by the co-precipitation technique with the post-oxidation annealing in air atmosphere. The process is explained below.

Zinc Chloride and NaOH powders of analytical grade purity were used as chemical reagents in the preparation of ZnO nanoparticles. Zinc chloride solution (0.2 M) was prepared in 20 mL ethanol by constantly stirring at 60°C for about half an hour. Then a separately heated 0.4 M NaOH solution at 60°C was slowly added to the above solution in order to initiate the chemical reaction. The following chemical reac-

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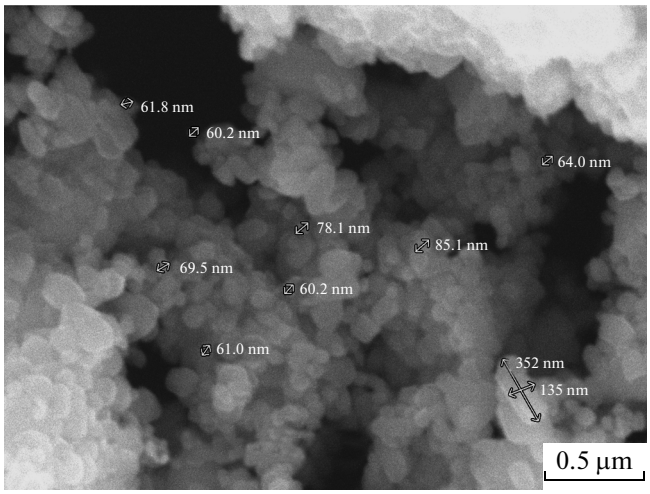


**Fig. 1.** SEM image of ZnO before laser shot.

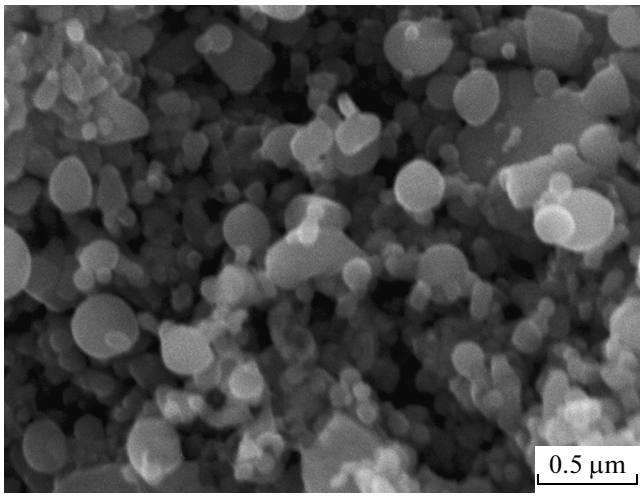


**Fig. 2.** SEM image of ZnO after laser shot.

tion took place in the process of fabrication of ZnO nano particles.

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl.$$

Zinc Hydroxide is insoluble, it would most likely form some sort of precipitate (ppt). Sodium chloride is soluble. After 1hr of constant stirring at 60°C, the product was allowed to come to room temperature. It was then centrifuged and washed 10 times with deionized water and two times with ethanol to remove the by-products. The final filtered product was then dried into solid powder at low temperature, grinded and finally annealed at 450°C to get ZnO nanoparticles. The reaction after drying is;

$$Zn(OH)_2 \longrightarrow ZnO + H_2O.$$

The ZnO nanoparticles were irradiated with one shot of laser beam of 6 ns pulse and 25 mJ energy from third harmonic of Nd: YAG laser system at wavelength of 355 nm.

## 3. RESULTS AND DISCUSSIONS

SEM images of the synthesized ZnO nanoparticles before and after laser irradiation are depicted in Figs. 1 and 2, respectively. The images reveal that after laser irradiation, the size of the particles are increased and agglomerated in different shapes. The XRD pattern shown in Fig. 3 suggests that the ZnO nanoparticles crystallize in Wurtzite structure (Hexogonal phase) and all the peaks match well with JCPDF file no. 36-1451, $a = 0.3249$ nm, $c = 0.5206$ nm. Increase in size of the particles is also observed as calculated from Scherrer relation before and after laser irradiation. Usually, the crystallite size calculated through Scherrer formula is smaller than the actual value as seen in SEM images. This is attributed to the widening of the XRD peak due to internal stress and defects [21]. The intensities of first three characteristic peaks (100), (002), and (101) almost reduced to half with substantial decrease in the broadening (FWHM) after irradiation of samples with laser beam at 355 nm. These effects are shown in Fig. 4. These effects indicate the improvement in the crystallinity or crystallite size of the samples after laser irradiation. Similar observation of improvement in crystallite size has been reported in literature when the ZnO nanoparticles were thermally annealed [22] as well as at 325 nm laser irradiated [20] ZnO QDs. The expansion and deformation of the

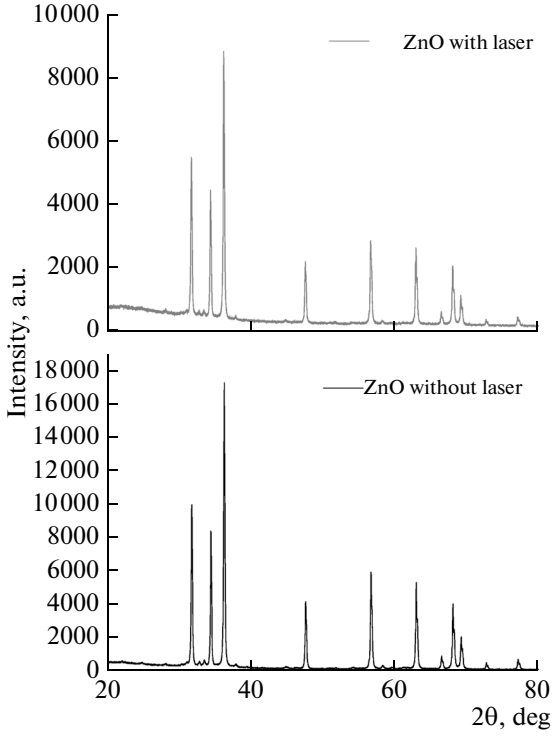


**Fig. 3.** XRD before and after laser shot.

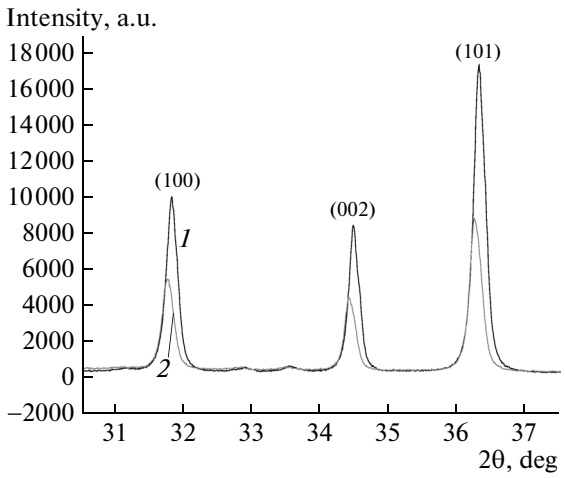


**Fig. 4.** Comparison of XRD peaks before (*1*) and after (*2*) laser irradiation.

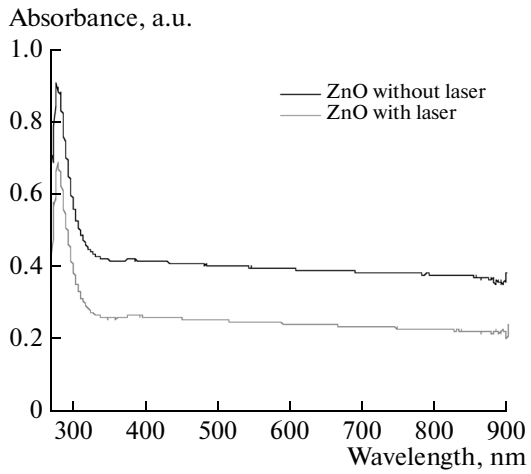


**Fig. 5.** Absorption spectra of ZnO nanoparticles before and after laser irradiation.

sample are attributed to the thermal effect caused by the localized surface Plasmon resonances [4].

Particle size of the crystallites size of the crystals in the sample before and after laser irradiation is calculated from XRD patterns using the following well-known Scherrer's formula [8]. The calculated values are given in table A.

$$D = \frac{0.9X\lambda}{\beta\cos\theta},$$

where $D$ is Crystallite size, $\lambda = 1.5405$ Å and $\beta$ is the broadening of diffraction line measured at FWHM in radians, and $\theta$ is the angle of diffraction.

Absorption spectra of ZnO nano powder before and after laser irradiation in the range of 250 to 900 nm are shown in Fig. 5. The absorption at higher wavelengths in the visible region is low and at wavelength 250–300 nm, an intense absorption is observed. Furthermore, it is recognized that all the absorption decreased for the whole range of 250 to 900 nm after the irradiation of laser. Similar results were observed by Shoutarou Takahashi et. al., using CW He–Cd laser of 325 nm and laser power of 50 mW. They claimed that the UV laser radiation increased the crystallinity at the ZnO nanoparticle surface by reducing the number of surface defects on the ZnO nanoparticles. This effect is confirmed in the above figures (Figs. 3, 4) and from the calculation using Scherrer's formula to estimate the increase in crystallinity (table). Actually, before laser irradiation, ZnO nanoparticles have large surface-to-volume ratio compared to the bulk materials. The nanoparticle surface has a greater influence on the material properties. Therefore, in our case by using the UV laser irradiation, the surface-to-volume ratio of the ZnO nanoparticles decreases which results in a decrease of in the absorption as shown in Fig. 5. Furthermore, we may expect increase in the transmission and decrease in the reflection as a result of decreasing the surface area of the ZnO nanoparticles. These results are confirmed from the transmission and reflection data as mentioned below.

The transmission spectra of ZnO nanoparticles were recorded in UV–visible near the infrared region (250–850 nm). Figure 6 shows the variation of transmittance with the wave length for ZnO nanoparticles. The average transmission in the visible region increases from 40 to 60% after irradiation. The absorption coefficient $\alpha$ was calculated from the transmission spectra using the equation,

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right).$$

The direct band gap of ZnO nanoparticles were calculated from Fig. 5 using the following Tauc's relation;

$$ah\nu = A(h\nu - E_g)^m,$$

where $\alpha$ is the absorption coefficient, $h$ is the Planck's constant, $\nu$ is the frequency of incident light, $E_g$ is the energy band gap of material and m is the factor governing the direct/indirect transition of electron from the valance band to the conduction band. Figure 7 demonstrates Tauc's plot of ZnO nanoparticles before and after laser irradiation. It was found that the band gap of ZnO nanoparticles decreased from 4.13 eV down to 3.96 eV and becomes narrower after laser irradiation. This reduction is also expected since the gap between valance band and conduction band decreases with

Calculated mean crystallite size of the sample from XRD patterns

| | FWHM | Crystallite size (Å) |
|---|---|---|
| ZnO NPs before laser irradiation | 0.27096 | 304.69 |
| ZnO NPs after laser irradiation | 0.22962 | 359.29 |

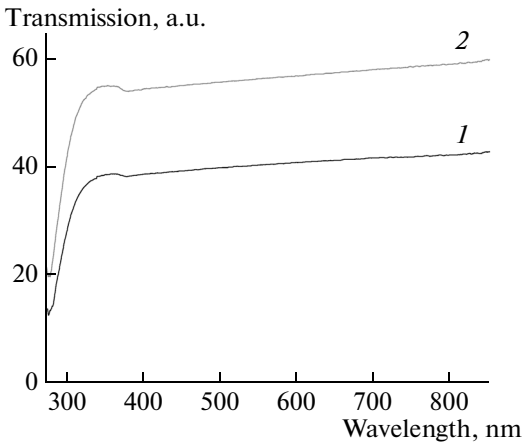


**Fig. 6.** Transmission spectrum of ZnO nanoparticles (*1*) before and (*2*) after laser irradiation.

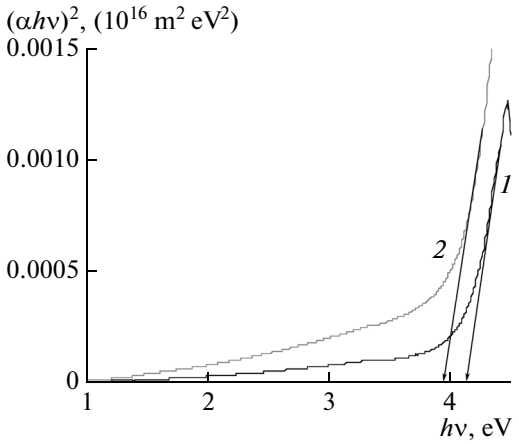


**Fig. 7.** Tauc's plot of ZnO nano particles (*1*) before and (*2*) after laser irradiation.

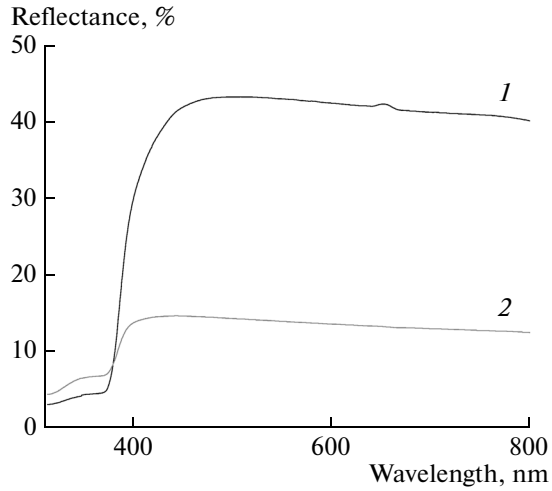


**Fig. 8.** Reflectance spectra of ZnO nano particles (*1*) before and (*2*) after laser irradiation.

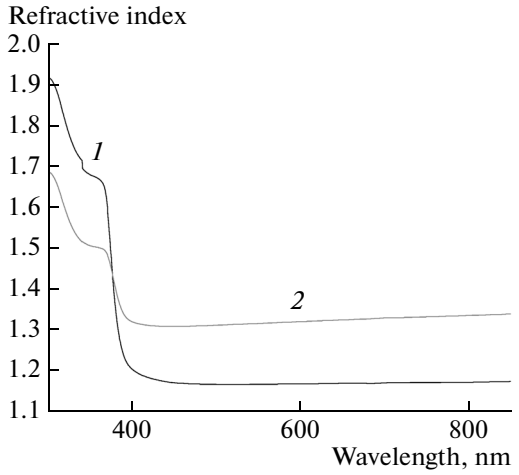


**Fig. 9.** Plot of refractive index as a function of wavelength, (*1*) before and (*2*) after laser irradiation.

increase of particle size [26] which confirms the explanation given above due to increasing the ZnO crystallinity.

Figure 8 shows the reflectance R before and after laser irradiation of ZnO nano powder. The spectra show that at lower wavelength range the reflectance of the ZnO nano powder increases before and after laser irradiation and becomes almost constant at higher range of visible region. The point where the reflectance becomes constant shifted to the shorter wavelength and deceases in the case of laser irradiation that also confirms our explanation given above due to increase in the ZnO crystallinity.

The refractive index can be determined using reflectance data with the following relation [23].

$$n = \sqrt{\frac{1+\sqrt{R}}{1-\sqrt{R}}}.$$

The refractive index ($n$) of before and after laser irradiated ZnO nano powder as a function of wavelength is shown in Fig. 9, the refractive index of ZnO nano powder before laser irradiation is 1.16 and after laser irradiation it increases to 1.32. It may be due to the increase in the crystalline size after laser irradiation.

The Photoluminescence (PL) spectra, measured by spectrofluorometer of ZnO nano powder at room temperature are shown in Fig. 10. It has also been observed that there are two crystal defects or defect levels at 399.86 and 422.18 nm, which might be associated with oxygen vacancies [24] and thus altering the path for de-excitation of electron. By irradiation of laser, the defect peaks have shifted slightly to the lower wavelength. We determined that the intensities of the defect peaks become weaker after laser irradiation [25].

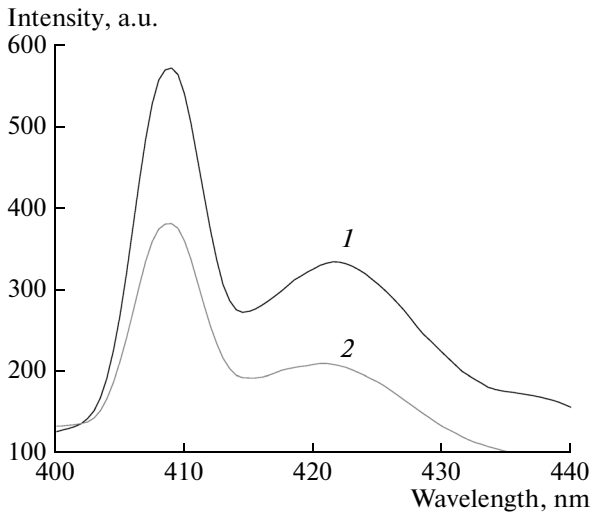


**Fig. 10.** PL spectra of ZnO nano particles (*1*) before and (*2*) after laser irradiation.

## 4. CONCLUSION

Nanoparticles of ZnO powder synthesized with co-precipitation technique are irradiated with UV laser. The observed results revealed the UV laser irradiation increases the ZnO nanoparticles crystallinity that affects the optical properties of the ZnO. The transmission increased while reflectance and absorbance decreased. Expansion and deformation in the nano dimensions are observed after laser irradiation. The band gap of the nanoparticles becomes narrower after the UV laser irradiation. Thus, the energy band gap can be controlled using UV laser, which represents an important result in semiconductors industrial applications.

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