Laser-Induced Synthesis of Pure Zinc Oxide Nanoflakes

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Abstract. Nanostructured zinc oxide (ZnO) has received immense attention as a low-cost and non-toxic photo-active material for different applications such as photocatalysis, photovoltaics, photonic and bio-medical fields. Herein, facile crystalline ZnO nanoflakes were prepared by homogeneous precipitation followed by laser-induced recrystallization and without the use of any organic ligand. The effect of laser type and wavelength on the recrystallization process was studied adopting a pulsed nitrogen laser (λ=337 nm) and a continuous argon laser (λ=488 nm). The pulsed nitrogen laser features a pulse duration of 150±1 ns, pulse energy of 1.3±0.3 mJ, and a target irradiance of 5.7±0.5 kW/cm² while the continuous argon laser provides an irradiance of 10±0.3 mW/cm². The morphology, structure and optical properties of the prepared nanostructures were studied using a scanning electron microscope (SEM), X-ray diffraction (XRD), UV-Visible, photoluminescence (PL), and Raman spectroscopy. The results confirm the formation of pure ZnO nanoflakes of the wurtzite structure. The laser-induced evolution of ZnO nanoflakes depends on the nature of the precipitating agent, laser energy and exposure time. The ZnO nanoflakes prepared using urea-assisted homogeneous precipitation is more advantageous than that precipitated with NaOH. Moreover, the pulsed nitrogen laser of higher irradiance demonstrated an enhanced formation of ZnO nanoflakes after 90 min of irradiation. The laser irradiation provides a facile synthetic route to pure ZnO nanostructures for various applications.

1. Introduction
Zinc oxide is one of the most important, abundant and environment-friendly metal oxides that has been extensively investigated and employed as a photoactive semiconductor material in different fields such as photovoltaics, photocatalysis, optoelectronics, gas sensing, and biomedical applications. Zinc oxide-based materials absorb light energy in the UV region and provide high resistance to photo corrosion, low cost, and lack of toxicity in addition to their antimicrobial and antibacterial activity. [1-4] Tailoring the morphology of ZnO nanostructures have received significant attention as an approach to modify the physical and chemical properties of ZnO particles. In recent years, laser irradiation of solid and fluid targets using pulsed or continuous laser sources has been shown as an attractive and simple method that has shown great success for the fabrication of various inorganic nanostructures of controllable size, shape, and properties such as zinc oxide nanomaterials. [5-8]
The laser treatment of the surface or bulk materials not only can remove undesired surface contaminants but also can result in the formation of unique architectures and enhanced quality of different types of nanomaterials.[9-11] Because of the unique ZnO properties and importance in various fields, the development of a simple and efficient laser treatment approach to induce recrystallization and shape evolution of ZnO nanostructures upon interaction with a laser would be highly desirable. Meng N. et al. studied the effects of annealing and laser irradiation on optical and electrical properties of ZnO thin films and found the ZnO thin films annealed by laser irradiation from a pulsed KrF excimer source (248 nm) exhibited different surface morphology compared to calcined ZnO samples.[12] T. Shimogaki et al. reported the fabrication of ZnO nanowires with diameters of several dozen nanometers by UV laser (KrF excimer) annealing of ZnO particles grown on buffer ZnO layer using a pulsed laser.[13] In addition, the laser annealing has been shown to improve the optical properties of laser-annealed ZnO nanorods compared to that thermally-annealed particles.[7]

Herein, we report a promising laser irradiation method that can result in substantial shape evolution of ZnO nanoparticles in limited processing time. The facile laser-assisted synthesis of unique ZnO nanoflakes can have great potential in many applications including optical, sensing and biological applications.

2. Materials and Methods

2.1. Wet Chemical Synthesis

The different ZnO nanoparticles were synthesized by the homogenous precipitation under alkaline conditions followed by thermal calcination or laser-induced recrystallization in ambient air. In a typical experiment, precipitates of hydrated zinc hydroxide were prepared by homogenous precipitation in alkaline conditions using two different precipitating agents, namely urea and sodium hydroxide. For the urea-assisted homogenous precipitation, typically 0.0336 moles of zinc nitrate hexahydrate (96%, LOBA, Chemie) was dissolved in 60 ml distilled water and the solution was sonicated for 10 min. A solution of 0.336 moles of urea in 60 ml distilled water was prepared by sonication and was added to the aqueous solution of zinc nitrate. The mixture was stirred for 180 min using mechanical hotplate/stirrer and pH was adjusted to 10 with 0.2 M sodium hydroxide solution. To allow the hydrolysis of urea, the reaction mixture was kept under stirring at 90 °C for 6 h until the urea-assisted homogenous precipitation is completed. Afterward, the precipitated particles were separated with centrifuge, washed several times with distilled water and finally were dried in an electric oven overnight. For the preparation of zinc oxide using sodium hydroxide in absence of urea, typically, 0.0336 moles of zinc nitrate hexahydrate and equal moles (0.0336 moles) of trisodium citrate were dissolved in 200 ml distilled water and the solution was sonicated for 10 min. A solution of 0.0672 moles of sodium hydroxide in 50 ml distilled water was added to the zinc nitrate-sodium citrate solution and the mixture was sonicated for 10 min and stirred for 2 h until complete precipitation. The precipitate was separated with centrifuge and washed several times with water and was finally dried in an electric oven overnight. For thermally annealed particles, the dried product particles were calcined in an electric muffle furnace in ambient air at 300 °C for 2 h with a heating ramp rate of 5° min⁻¹.

2.2. Laser-Induced Recrystallization

The laser-induced recrystallization of as-prepared ZnO particles was carried out using two different laser systems. The two lasers that were used are namely a pulsed nitrogen (N₂) gas laser and a continuous argon (Ar) gas laser. The two different lasers were chosen to investigate the effect of the laser type, laser wavelength and laser irradiance on the physicochemical characteristics of ZnO particles including morphology and crystal structure. The pulsed N₂ laser (Ruhr University Bochum, Germany) features a wavelength of 337±1 nm, a pulse duration of 150±1 ns, and a pulse energy of 1.3±0.3 mJ. The N₂ laser beam was focused onto a spot area of 1×1.5±0.2 cm² using a quartz cylindrical lens with a focal length of 15 cm. The irradiance of the pulsed N₂ laser beam at the sample surface is 5.7±0.5 kW/cm².
The continuous Ar laser (Spectra-Physics, Model 183-C0201) is a multi-power system from 10–70 mW and a beam diameter of 0.7 mm with a selected wavelength of 488 nm. The Ar laser beam diverged into a spot beam of 1 cm diameter using a biconcave quartz lens of focal length 10 cm. The Ar laser beam provided an irradiance of 10±0.3 mW/cm² at the sample surface. For the irradiation of thin solid film samples, the as-prepared ZnO particles were deposited on a glass substrate with a layer thickness of 0.4 mm that was positioned on a holder in the front path of the laser beam. In another experiment, an aqueous suspension of the as-prepared ZnO sample was irradiated in a 1 cm-thick quartz cuvette to study the effect of the surrounding medium. The laser irradiation of the aqueous suspension was conducted under continuous mechanical stirring to ensure a homogenous exposure to the laser beam. In all laser irradiation experiments, samples were irradiated in a dark room to eliminate any effects due to the background light.

![Figure 1. A sketch of the experimental set-up used for the laser irradiation of as-prepared samples in the case of (a) thin-film solid sample, and (b) an aqueous suspension of as-prepared ZnO particles.](image)

2.3. Characterization

The different products were characterized by standard physical techniques. Scanning electron microscopy (SEM) images acquired using Quanta FEG250 scanning electron microscope. The powder X-ray diffraction (XRD) measurements were carried out at room temperature using X’pert diffraction system (Philips, Holand) with Cu–Kα1 radiation at 40 kV voltage, electrical current 30 mA, and a scanning speed of 0.03° per minute from 5° to 80°. The identification of crystal structures of prepared materials was based on the database of the Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data (JCPDS-ICCDD) system. Raman spectra were recorded using LabRAM HR Evolution Raman Spectrometer (HORIBA Scientific, France) which is equipped with a 532 nm laser source for excitation. The spectrum acquisition consisted of 10 accumulations with an acquisition time of 5 sec, the grating spectral resolution of 300 and 5% neutral density (ND) filter. UV-visible absorption spectra of aqueous suspensions of the prepared samples have been measured using Ocean Optics spectrometer model (HR4000 UV–NIR) with spectral resolution of 1nm and equipped with an optical fiber (2 m long, 400 µm core diameter, buffer/coating by polyimide, jacketing by mono–coil and with two premium-grade SMA 905 Connector -QSMA). Absorption spectra were recorded in the range of 200 – 1100 nm using the Toshiba TCD1304AP linear CCD array detector. The Photoluminescence measurements have been carried out using an F-7000 spectrofluorimeter with an excitation wavelength of 340 nm and a scan range from 350 to 900 nm.

3. Results & Discussion

3.1. Morphological Properties

Scanning electron microscopy (SEM) is one of the most important techniques used to study the morphology of nanomaterials.[15] Figures 2,3 compare the effects of thermal calcination and laser-induced recrystallization and annealing on ZnO particles prepared with homogenous precipitation under alkaline conditions using urea and NaOH. The SEM images of the ZnO nanoparticles obtained using urea and NaOH followed by thermal calcination at 300 °C for 2 h (Figure 2) reveal agglomerates of large particles with uniform semispherical morphology in case of particles prepared with urea-assisted homogeneous precipitation (Figure 2-a,b) and non-uniform shape for particles prepared with NaOH.
The 10th International Conference on Laser Applications (ICLA 10)

For the ZnO particles precipitated using urea and NaOH and annealed with laser irradiation using pulsed N\textsubscript{2} laser (337 nm, target irradiance \(\sim 5.7\) kW/cm\textsuperscript{2}) for 90 min (Figure 3), the laser-induced recrystallization resulted in significant change of the surface morphology of the ZnO particle and the shape evolution to well-defined ZnO nanoflakes. The SEM images shown in Figure 3 reveal the large lateral dimensions of the ZnO nanoflakes which are in the micrometer length scale in both ZnO precipitated by urea (Figure 3-a,b) and by NaOH (Figure 3-c,d). When Ar laser (488 nm) was used for irradiation, the shape evolution to ZnO nanoflakes was observed after 180 min of continuous Ar laser irradiation with a target irradiance of \(\sim 10\) mW/cm\textsuperscript{2}, as can be seen in Figure A1. The relatively long-exposure time (180 min) encountered in the case of using Ar laser for treatment compared to the pulsed N\textsubscript{2} laser (90 min) is due to the difference in energy and irradiance at the sample surface compared with N\textsubscript{2} laser. The SEM images displayed in Figures 2, 3 & A1 indicate the substantial influence of both pulsed N\textsubscript{2} laser (337 nm) and continuous Ar laser (488 nm) on the formation of ZnO nanoflakes thin films which are distinct in shape and lateral dimensions from ZnO annealed with conventional thermal heating. Unlike ZnO nanoflakes obtained by irradiation of ZnO solid thin films, when the N\textsubscript{2} laser treatment was performed on an aqueous suspension of ZnO sample prepared by urea instead of ZnO thin films, the fewer number of ZnO nanoflakes could be observed along with non-uniform aggregates of ZnO particles. This could be due to the dissipation of the laser energy owing to the continuous mechanical stirring of particles suspended in water. The SEM results indicate that using urea as the precipitated reagent is more advantageous due to a high surface modification process which eliminates more agglomeration during synthesis and controls the morphology of adjacent particles by self-assembly and shape transformation.[16-19]

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3.2. Crystal Structure (XRD Properties)

Figure 4 displays the X-ray diffraction patterns obtained for different samples including as-prepared ZnO prior to laser irradiation and ZnO samples irradiated with N$_2$ (UV) and Ar (Visible) lasers for different exposure times. The XRD results indicate the main diffraction peaks of (100), (002) and (101) growth planes of ZnO which are in match with those in the reference pattern (Card JCPDS No. 01-076-0704) of the calculated spectrum of hexagonal zinc oxide. The laser irradiation with pulsed N$_2$ laser for 90 min and with continuous Ar laser for 180 min led to comparable laser-induced recrystallization as indicated by the oriented growth manifested by the XRD reflection peak at about 32.6°. The XRD results together with the SEM results shows the obvious modification of the crystal growth and shape of the irradiated ZnO nanoparticles leading to the formation of well-defined ZnO nanoflakes. The N$_2$ laser used for irradiation in the UV region is strongly absorbed by the ZnO thin film material than the Ar laser that is in the visible region and such energy could modify the surface and increase the crystallinity.[20] The laser-induced recrystallization results in a larger crystalline domain and increased lateral dimensions by shape transformation from semi-spherical aggregates to nanoflakes due to self-organization and oriented attachment driven by laser treatment.[21]
3.3. UV-Visible Absorption Properties

The UV-visible absorption spectroscopy is a very essential technique to study the optical properties of the different nanoparticles. It provides information on the shape and the size of the nanoparticles and how they affect the optical band gap and the band structure that control the absorption properties of the materials.[22, 23] Figure 5 compares the absorption spectra of the different prepared ZnO nanoparticles that were annealed by conventional heating and by laser irradiation using pulsed N₂ laser and continuous Ar laser as laser excitation sources. The absorption spectra of the as-prepared ZnO nanoparticles precipitated using urea and NaOH exhibit two absorption peaks in the UV region. The first absorption peak is observed in the range of 260-278 nm which lies below that of bulk ZnO that is typically around 388 nm [24, 25] The blue-shift of the absorption peak could be attributed to the formation of nanoparticles with smaller crystallite size compared to bulk counterpart. The second absorption peak was observed in the region between 364-374 nm and can be ascribed to the presence of ZnO agglomerates like bulk ZnO counterpart. The relatively sharper profile of the first absorption peak can be related to the larger number of individual nanoparticles or nanoflake compared to the fraction of agglomerated particles that behave like the bulk particles and vice versa. The UV-visible absorption spectra of ZnO particles prepared by urea-assisted homogenous precipitation prior to and upon thermal or laser annealing are compared in Figure 5,a-e. In the case of as-prepared ZnO before thermal annealing or laser annealing (Figure 5-a), a broad absorption peak centered around 277 nm and a sharp peak positioned at about 370 nm are observed. These absorption features indicate the larger fraction of individual nanoparticles relative to that of the remaining bulk. The absorption of the sample obtained after the Ar laser irradiation of solid ZnO film for 180 min (Figure 5-b) is characterized by a broad absorption band at 288 nm and a narrow absorption band at around 364 nm. This indicates the smaller fraction of the formed nanoflake relative to that of the ZnO aggregates. As can be seen in Figure 5-c, the absorption spectrum of the sample obtained after the N₂ laser irradiation of an aqueous ZnO mixture for 90 min displays absorption a broad peak at about 298 nm and a sharp peak at around 370 nm. On the other hand, the N₂ laser irradiation of solid ZnO film for 90 min gives rise to a sharp absorption peak at 262 nm and a broader peak at about 368 nm, as can be seen in Figure 5-d. This indicates the enhanced formation of ZnO nanoflakes with larger lateral dimensions and higher fractions relative to agglomerated ZnO particles. The absorption spectrum of the thermally-annealed sample shown in Figure 5-e exhibits two sharp peaks at around 270 nm and 372 nm indicating the smaller fraction of the nanoparticles and the higher fraction of aggregated particles due to sintering. Figure 5-f,g represents the absorption spectra of the NaOH-precipitated ZnO solid films upon irradiation with N₂ laser for 90 min and after thermal annealing. Both absorption spectra possessed a sharp absorption peak at 275 nm and a broad peak at 368 nm. This indicates the smaller fraction of the ZnO nanoflakes or nanoparticles after laser annealing or thermal annealing, respectively, compared to that of the aggregated particles. Based on the UV-visible absorption and SEM results, it can be concluded that urea-assisted homogeneous precipitation followed by laser irradiation using pulsed N₂ laser provides a facile inorganic synthetic route to the controlled preparation of ZnO nanoflakes.[16-18] The urea-assisted precipitation allows better control over the improved formation of ZnO nanoflakes due to the slow gelation process derived by slow chemical decomposition of urea and the gradual rise of pH of the reaction mixture.[19] This slow gelation led to controlled growth and minimized particle agglomeration during synthesis with a higher degree of control over the morphology. Likewise, the pulsed N₂ pulsed laser with high irradiance at the sample surface is more efficient toward the laser-induced recrystallization processes compared to the continuous Ar laser as confirmed by the morphology and structure results.
3.4. Optical Bandgap

Absorption spectroscopy is commonly used as an analytical tool for studying the interactions between electrons and UV-visible light radiation. The fundamental absorption process refers to the band-to-band transitions and it manifests itself by a rapid rise in the absorption that can be used to determine the optical bandgap of the material. The absorption coefficient ($\alpha$) is related to the absorbance ($A$) according to the Beer-Lambert law where,

$$\alpha = \frac{1}{d} \ln \frac{I_0}{I} = \frac{2.303}{d} \log \frac{I_0}{I} = \frac{2.303 A}{d}$$

where ($A$) is the absorbance and (d) is the sample thickness.

The absorption coefficient of many amorphous materials ($\alpha$) is related to the optical band gap ($U_g$) through Tauc and Davis-Mott model.[22]

$$(\alpha h\nu)^n = \beta (h\nu - U_g)$$

where (n) is a constant and (\beta) is the exponent constant index.

The four types of transition in amorphous materials are namely, directly allowed, directly forbidden, indirectly allowed and indirectly forbidden transitions. These transitions are represented with (n) equal to 2, 2/3, 1/2, and 1/3 respectively. The experimental data from the dependence of $\alpha h\nu = f(h\nu)$ are fitted according to equation (2). For ZnO, the linear dependence of $(\alpha h\nu)^n$ versus $h\nu$ is accordingly obtained for n=2. This indicates that near the absorption edge, the electronic transitions are directly-allowed and do not involve phonons.[26-28]

The Tauc plots used to determine the optical bandgap of the differently prepared ZnO samples are displayed in Figure 6. The calculated energy bandgap based on the first absorption peak ranged from 2.95 eV to 3.9 eV depending on the size of the nanoparticles or nanoflakes where the energy band gap is inversely proportional to the size.[24, 25] On the other hand, the energy bandgap based on the second absorption peak ranged from 2.75 eV to 3.05 eV according to the degree of agglomeration during synthesis and upon thermal annealing or laser-induced recrystallization. The calculated energy bandgap values indicate that urea as an alkaline precipitating agent is more advantageous than sodium hydroxide in obtaining small nanoparticles with less agglomeration. In addition, the pulsed N\textsubscript{2} laser with relatively high irradiance at the sample surface is more efficient in the recrystallization processes than Ar laser.
Figure 6. Tauc plots used to determine the optical bandgap for different ZnO samples. (a) thermally-annealed ZnO (Urea) (b) N2 laser-irradiated ZnO-(Urea) in solution, (c) N2 laser-annealed ZnO (Urea) thin film, (d) thermally-annealed ZnO (NaOH) thin film, (e) N2 laser-annealed ZnO-(NaOH) thin film and (f) Ar laser-annealed ZnO-(Urea) thin film.

3.5. Photoluminescence and Raman Characteristics

The photoluminescence (PL) originates from the recombination of surface states where the strong photoluminescence indicates that the surface states remain very shallow.[29-31] The photoluminescence (PL) spectrum of ZnO nanoflakes prepared by N2 laser irradiation of ZnO (urea) thin film for 90 min is shown in Figure A3. The PL spectrum exhibits two emission peaks, one dominant emission peak centered around 385 nm and a small shoulder peak at around 412 nm. The dominant emission peak at 385 nm is attributed to the near band gap excitonic emission of the ZnO nanoflakes and the shoulder emission peak at around 412 nm could be ascribed to the recombination events within the agglomerates or the bulk ZnO nanoflakes.[29] The emission peak arise from the transition of a photo-generated electron from the conduction band to a deeply trapped hole.[30, 31]
Raman spectroscopy is a very useful tool to gain information about the electronic properties of semiconductors and oxide materials.\cite{32,33} The Raman spectra of the ZnO nanoflakes prepared by N$_2$ laser irradiation for 90 min using urea and NaOH as precipitating agents are shown in Figure A4. The wurtzite-structured (hexagonal) ZnO belongs to the C$_{6v}$ space group having two formula units per primitive cell with all the atoms occupying the C$_{3v}$ sites. There are eight sets of zone center optical phonons, namely A$_1$ and E$_1$ modes which split into transverse (A$_{1T}$ and E$_{1T}$) and longitudinal (A$_{1L}$ and E$_{1L}$) optical phonons and the E$_2$ mode that consists of two Raman active modes of low- and high-frequency phonons (E$_{2L}$ and E$_{2H}$).\cite{34,35} As can be seen in Figure A4, the Raman spectra of ZnO nanoflakes prepared by laser-induced recrystallization using N2 laser (337 nm) as excitation source are featured with the main peak at 435-437 cm$^{-1}$ due to the E$_2$ Raman mode characteristic of ZnO with a hexagonal crystal structure. The high intensity and sharp peak of E$_2$ mode at 435-437 cm$^{-1}$ with other observed peaks demonstrate that the laser-prepared wurtzite ZnO nanoflakes are of good crystallinity as confirmed by the XRD results shown in Figure 4.

In summary, the results indicate the size and shape of the ZnO nanoparticles were significantly influenced by the annealing method as well as the chemical precipitating agent used to assist the homogenous precipitation of the hydrated zinc oxide particles. The laser-annealed ZnO materials exhibited architectural morphology different from those annealed by conventional thermal treatment due to the favorable growth of unique crystallographic planes or defects due to recrystallization driven at the surface by laser irradiation.\cite{5} The shape evolution by irradiation from N$_2$ laser ($\lambda=337$ nm) on solid ZnO thin films and on aqueous ZnO suspension is described. The laser treatment results in a modification and shape evolution into well-defined nanoflakes while maintaining the crystalline nature of the particles. Optimal irradiation parameters in terms of exposure time to produce maximum lateral dimensions of the ZnO nanoflakes were identified and the behavior under pulsed N$_2$ laser irradiation was compared with that of continuous Ar laser irradiation ($\lambda=488$ nm). Scanning electron microscopy, X-ray diffraction, and optical spectroscopy were further employed to confirm the topological, structural and electronic properties of the ZnO nanoflakes prepared by laser irradiation and consequent oriented growth.

4. Conclusions
In conclusion, the dependence of the morphology, structural and optical properties of ZnO nanoparticles on both the chemical precipitation route and the annealing method was studied. The laser-induced recrystallization for the ZnO particles prepared using urea led to shape evolution and formation of ZnO nanoflakes. The urea precipitating agent exhibit better control of the chemical precipitation and gelation process compared to NaOH. The pulsed N$_2$ laser (337 nm) of high irradiance at the sample surface (5.7 kW/cm$^2$) led to enhanced formation of ZnO nanoflakes with larger lateral dimensions compared to the Ar laser (488 nm) of lower irradiance (10 mW/cm$^2$) at the target. The results confirm the effective N2 laser-induced recrystallization processes after laser exposure of 90 min leading to shape evolution into well-defined ZnO nanoflakes.

Acknowledgments: The authors acknowledge using Cairo University Facilities at NILES, Physics Dept. and at EGNC.
Appendix

Figure A1. SEM images of ZnO nanoflakes prepared by laser-induced recrystallization of urea-precipitated ZnO thin films using continuous Ar laser (488 nm) exposure for 180 min.

Figure A2. SEM images of ZnO prepared by laser irradiation of an aqueous suspension of urea-precipitated ZnO particles using pulsed N\textsubscript{2} laser (337 nm) for 90 min.

Figure A3. Photoluminescence spectrum of ZnO nanoflakes using an excitation wavelength of 340 nm.

Figure A4. Raman spectra of ZnO prepared by N\textsubscript{2} laser irradiation for 90 min using (a) urea and (b) NaOH as precipitating agents.
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