Generation of nano-scaled Zinc oxide hexagonal crystals by pulsed laser fragmentation of Zinc oxide micro-spheres

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We report the formation of well-defined ZnO nanostructures using pulsed-laser fragmentation of Zinc oxide micro-spheres in water condition. The typical morphology of the ZnO nano-particle exhibits hexagonal crystal structure with sides approximately 30nm. The occurrence of an inhomogeneous light intensity distribution on ZnO micro-spheres is responsible for the laser micro-etching/fragmentation process, resulting in the curvilinear arrays of the nano-scaled ZnO hexagonal crystals.

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1. Introduction

ZnO micro- and nano-scaled particles [1-5] with distinctive geometrical shapes have been intensely pursued in recent decades due to their enormous potential for technological applications such as fast responsive sensor, optoelectronic and photo-catalytic device, etc [2-3, 6-7]. As one of many challenges in the design and synthesis of ZnO nano-particle, the centre-symmetric geometrical structure with well defined morphologies represents a very important category, which is an important objective of fundamental and applied research. Among all available synthesis methods (such as chemical vapor deposition (CVD), thermal evaporation [4, 7], metal catalysts [7], sol-gel-based approaches, [1] spray-drying and gas-blowing [1], etc), laser sintering and fabrication technology [3, 6, 7-10] characterized by one-step fabrication of nano-structures with economy of time and material has attracted much attention. For example, by using excimer laser ablation in an water-ethanol mixtures with SDS (sodium dodecyl sulfate) as surfactant, Yan *et al*. reported the self-assembly of ZnO_x nanoclusters into hollow nanoparticles [3]. While, only dispersed nano-layers could be obtained without ethanol [4]. Note that, in many cases, the appropriate liquid medium (e.g. aqueous/nonaqueous liquid or solution with surfactant) plays an important role in the fabrication of well defined nano-structures. Meanwhile, some byproducts were brought in nano-material generation from bulk materials, since the reaction occurs between metal species and activated solution.

Recently, we reported experiments [9-10] in which arrays of ZnO micro-spheres with well faceted structures were fabricated by laser ablation of Zn metal in the presence of oxygen background gas. On the other hand, the formation of laser induced nano-structures in water have relied upon the inhomogeneous energy deposition that result from the existence of surface roughness with amplitude less than the wavelength of the laser light [7]. Therefore, if one can optimize the subsequent laser beam to focus on the ZnO micro-spheres, and provide the facets on ZnO micro-spheres to be small compared to the wavelength laser beam, then the inhomogeneous energy deposition will be occur, resulting in laser localized melting/fragmentation. In this paper, we will take full advantage of the polygonal facets formed on ZnO micro-core, and report the formation of well-defined ZnO nano-scaled structures by pulsed laser fragmentation of ZnO micro-spheres in pure water without use of catalysts or additives. Meanwhile, a detail discussion of the growth mechanism is addressed. The aim of this work is to inspire deeper investigations for generating more complex structures by this strategy.

2. Experiment setup

The experimental condition has been described in our previous studies [9-10]. Brief, we chose a well polished pure (99.99%) zinc metal as the target. The surface modifications were obtained by multi-pulses laser irradiation in vacuum condition (~3Pa) with Gaussian profile from a Nd:YAG (yttrium aluminum garnet) laser (Quanta Ray, Spectra Physcis). The laser beam was operated in fundamental IR (1064nm) mode, with 10 Hz repetition rate and 10ns FWHM pulse duration. The laser beam was focused on zinc metal by a quartz lens (L1) with a 90mm focal length. Another 50 mm quartz lens (L2) was

used to image the laser-induced plasma with size of 1:1 on the 10 μm wide entrance slit of a spectrometer system. The spectral lines of Zn atoms in laser ignited plasma were recorded by a charge-coupled device (CCD) chip (700× 1340 pixels) at distance of 4mm to the target surface. The surface modifications and micro-structures were examined by mean of field emission scanning electron microscope (Hitachi High-Tech) operated at 15kV. Then the laser irradiated regions were immersed in pure water on the bottom of a rotating glass holder. The sequent laser beam was focused on the irradiated region by a quartz lens (L3) with a 111mm focal length. The power densities of the pulsed laser used in this experiment varied from ~14GW/cm^2 to ~18GW/cm^2, which was monitored by an energy meter (Molectron, EPM1000). After ~6×10^3 pusles (10 minute, 10 Hz) laser ablation, the nano-scaled ZnO particles in water were collected and characterized by transmission electron microscope(TEM, JEM-1011).

3. Results and discussion

Fig. 1 (a) shows the SEM image of the numerous micro-spheres formed on inner surface of the crater by 100 cumulative pulses laser (~15GW/cm^2) in vacuum condition. Then, the energy-dispersive spectroscopy (EDS) was carried out to determine the chemical composition of the representative micro-sphere. The result of EDS in Fig. 1(b) shows that the outer surface of micro-sphere is made of Zn and oxygen only, and the ratio of Zn to O is about 5:2. The low oxygen pressure in target chamber is a crucial factor for the formation of Zn-rich particles, which has been verified in previous work [9].

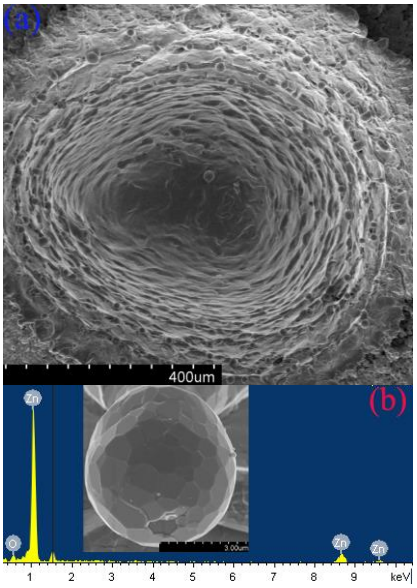

Fig. 1. (a) The numerous micro-spheres are formed on inner surface of the ablated spot on Zn target produced by 100 pulses laser (incident intensity ~ 15GW/cm^2) (b) the energy dispersive spectrum on a representative micro-sphere indicating the presence of zinc and oxygen only.

Before discussing the ZnO nano-structures fabricated in pure water, it is necessary to reveal the formation of polygonal facets on ZnO micro-core. The laser irradiated region covered with ZnO micro-spheres was produced by 1, 5 and 10 pulses laser (~15GW/cm^2) in vacuum condition. The sequence presented in Fig. 2 (a, b, c) shows the evolution of regular pentagonal and hexagonal facets on ZnO micro-core. When the single pulse laser beam was used, the high-magnification SEM image in Fig. 2(a) indicates that the ZnO spherical-shaped structure with diameter of ~1.9μm, exhibiting rather smooth surface. After five pulses ablation, some changes occurred on the ZnO micro-core surface, as shown in Fig. 2 (b). We note that some regular facets with sides approximately 400 nm were formed on the top surface of ZnO micro-core. Moreover, numerous nano-liquid drops (30~50nm) are accreting onto the facets. As for ten pulses laser used in this paper, the ZnO micro-sphere became completely covered with clear pentagonal and hexagonal facets, as observed in Fig. 2(c). To reveal the growth mechanism of polygonal facets on ZnO micro-core, laser etching and re-modification, as well as the gradient of surface tension have been proposed. Once the ZnO micro-core is formed by the first laser pulse, subsequent growth should be accomplished by preferential re-deposition of superheated material, and followed by laser sintering of liquid particles at tip region of the core. The presence of subsequent laser re-modification will facilitate heterogeneous nucleation of secondary nano-layers. Rapid cooling due to the expiration of the pulse, results in the gradient of surface tension at the curved region of ZnO micro-core, which is partly reason for the formation of the polygonal facets on tip region. The probable role of these liquid drops in Fig. 2(b) is to concentrate the laser beam by multiple reflections on facets surface. In this way, laser micro-etching is intensified at the surface region. The dynamic process of preferential re-deposition and subsequent laser etching/sintering will takes place on ZnO micro-core surface for increasing laser shots. On the other hand, the average diameters of these micro-spheres were measured as a function of the number of laser pulses, as shown in Fig. 2(d). The diameters of micro-spheres significantly increase from ~1.9μm to 8.5μm as the laser shots change from single to ten pulses, and then slightly increase to ~10μm after 25 cumulative pulses, finally remain practically constant for further increase the number of laser pulses. Then, 25 cumulative pulses were adopted in the following experiments, in order to provide stable ZnO micro-structures for laser fragmentation in water condition.

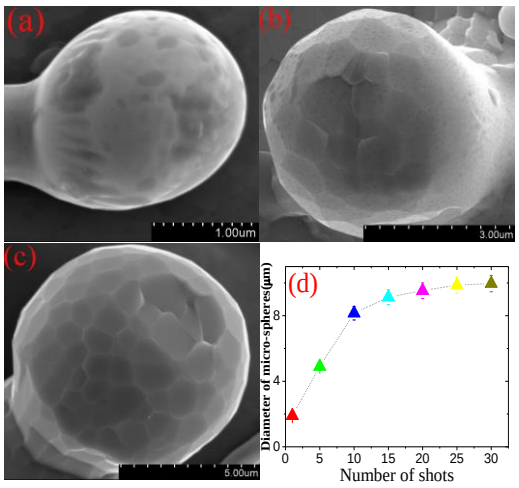

Fig. 2. (a-c) The typical ZnO spherical-like microstructures by 1, 5 and 10 pulses laser beam ablation at intensity of 15 GW/cm^2 under pressure of 3Pa. (d) The average diameters of these micro-spheres as a function of the number of laser pulses.

In next set of experiments, the pulses laser beam was focused on Zn irradiated area, and the targets were immersed in pure water. Two typical samples (denoted by sample (I) and sample (II)) were selected in the paper, sample (I) referred to ZnO micro-spheres with diameter of ~9μm by pulses laser ablation (power intensity~14GW/cm^2) in vacuum condition, and sample (II) corresponded to numerous ZnO micro-spheres with diameter of ~13μm by laser ablation at ~18GW/cm^2. After cumulative pulses (about ~6×10^3 pulses) laser fragmentation of sample (I) in pure water, the typical SEM image of ZnO micro-spheres on irradiation region is shown in Fig. 3(a).

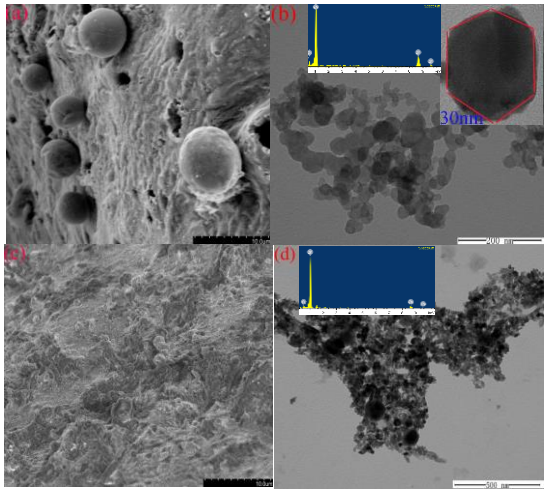

Fig. 3. (a) (c) SEM images of ZnO micro-spheres after subsequent pulses laser beam focused on the sample (I) and (II), respectively. (b) (d) typical TEM images of ZnO nano-structures in pure water created by pulses laser fragmentation of the sample (I) and (II), respectively; their corresponding EDS images are in the insets.

The observed result clearly indicates that the regular polygonal facets on ZnO micro-cores were completely separated from the cores after pulses laser fragmentation in water condition. Then the dissolvent of the ZnO particles was carefully examined by transmission electron microscope (TEM). Some more fascinating nano-structures are observed in Fig. 3(b). Numerous well defined ZnO polygonal nano-structures rotated, bended, and aggregated into curvilinear strings. The inset image in Fig. 3 (b) indicates that the typical morphology of ZnO nano-particle is characterized by hexagonal crystal structure with sides approximately 30nm. One important feature is apparent: The ZnO micro-spheres covered with regular facets can be fragmented by pulsed laser in pure water, dividing in to the micro-core on target and well defined nano-scaled hexagonal crystal structures in liquid. As shown by the inset of Fig. 3 (b), the energy-dispersive spectroscopy (EDS) confirms that the outer surface of the hexagonal crystal is made of Zn and O only. The proportion of oxygen stands at about forty percent, which is consistent with the measurement of ZnO micro-sphere in Fig. 1 (b). The findings suggest that H and OH ions seem not necessary for the formation of ZnO hexagonal crystal by laser fragmentation of micro-spheres in water condition. The mechanism of laser fragmentation is likely to be more physical in nature, and the high temperature and high pressure by laser induced evaporation in water would reasonable rather than chemical reaction [7, 11]. Compared with the laser ablation in vacuum condition, the hotter and dense plume with higher pressure can be generated at liquid-solid interface as the target immersed in water condition [7]. Therefore, the well-defined ZnO hexagonal crystal fabricated in this paper could nucleate directly from the fragments in the evaporation by laser focusing on the facets of ZnO micro-spheres. Meanwhile, it is worth noting that a very dramatic change in the micro-and nano-structures occurred when the irradiation was done on the sample (II), as shown in Fig.3(c) and (d). Both the regular facets and the ZnO micro-cores were ablated from irradiated surface after pulses laser beam focused on sample (II) in water. Numerous ZnO nano-particles with non-uniform sizes can not be separated from each other, and absorbed into micro-clusters with fabric-like structure. The structural development observed in Fig. 3(c) and (d) is very similarly to the productions by laser ablation of a bulk Zn metal in liquid environment. As shown by the inset of Fig. 3 (d), the radio of O and Zn elements measured by EDS spectrum is about 1:2, which is higher than that obtained in Fig. 3(b). The result suggests that OH, H, and their ions generated from the confining liquid rapidly dissolve into the laser induced plasma, and chemical reaction between these ions and laser induced metal material can occur then. Due to high density and temperature of the plasma, there is a sufficient supply of OH, H, etc, to keep the incorporation and diffusion mechanism going, and can enhance ZnO nuclei formation and growing. So the formation of ZnO micro-cluster is preferable to that of hexagonal crystal structures in the plasma during laser ablation of sample (II). It is obvious that laser ablation rather than laser fragmentation dominates when laser beam focused on sample (II) in pure water. The critical role of laser fragmentation is the existence of surface roughness with

amplitude less than the wavelength of the laser light [7], which will result in inhomogeneous energy deposition. In this paper, the surface roughness highly depends on the polygonal facets on ZnO micro-core. The most difference between samples (I) and (II) is the size of ZnO micro-sphere, resulting in different size of basic unit of facets on micro-core. To further verify the mechanisms of the observed results in Fig. 3, it is absolutely necessary to get insight into the basic unit of facets that is beneficial to understanding the laser fragmentation or ablation process in this paper.

In the following experiment, more extensive examinations were carried out to analyze the evolutions of the basic units as the laser intensities increase from ~14 GW/cm^2 to ~18GW/cm^2. The observed results are shown in Fig. 4(a-b), (c-d) and (e-f) for the power density of laser located at 14, 16 and 18GW/cm^2, respectively. The high-magnification morphologies presented in Fig. 4(b, d, f) clearly show that the units of polygonal facets are characterized by the truncated cone-shaped structure with circular cross section. As shown in Fig. 4 (a, c, e), the nano-scaled units with truncated cone structures and almost the same size have been cross-stacked one by one, and accreted on the ZnO micro-core. The radiuses of the smooth cross sections in Fig. 4(b, d, f) are calculated about 508, 784, 1380 nm for laser intensity located at 14, 16 and 18 GW/cm^2, respectively. The surface roughness of ZnO micro-sphere should be consistent with the measured size of the unit. It can be deduced that the surface roughness of ZnO micro-spheres on sample (I) is about 1000nm, which is less than the wavelength (1064nm) of the laser light used in this paper. In this way, pulses laser focused on sample (I) in water will provide inhomogeneous energy deposition on the facets of ZnO micro-spheres. As for the sample(II) used in this paper, the surface roughness of the ZnO micro-sphere is about 2600nm, which is about two times than the wavelength of the laser beam. The micro-sphere on sample (II) should be regard as a bulk target as following pulse laser focused in water condition. Micro-clusters other than well defined nano-scaled crystal structures were left in water, because laser ablation instead of laser fragmentation will play the important role in the laser-material interaction.

On the other hand, the well isolated spectral lines were collected from Zn species in expanding plasma generated in vacuum condition by subsequent laser beam (~15GW/cm^2) focused on three modified spots after cumulative pulses laser irradiation with intensities at 14, 16 and 18 GW/cm^2, respectively. As shown in Fig. 4 (g), the intensities of spectral lines from Zn atoms (468.01, 472.21 and 481.50nm) drastically increase as the subsequent laser focused on the modified spot by ~14 GW/cm^2 laser irradiation (sample(I)) changing to the ablated spot by ~18GW/cm^2 (sample(II)). For instance, the emission line at 481.50nm significantly increases from about 1.5×10^4 arbitrary units(a.u) to 4.8×10^4 (a.u) as the target changing from sample(I) to sample(II). It is well known that the intensity of spectral line in the expanding plasma is highly related to the laser ablation process. It can be deduced that laser ablation process rather than laser fragmentation play more and more important role when the subsequent laser beam focused on sample(II). As for sample(I), in contrast, laser fragmentation dominates in the laser-material interaction.

Based on the above discussions, if one could properly adjust the size of facets on ZnO micro-sphere (relative lower laser density, shorter laser wavelength, *i.e.* may be necessary), the laser fragmentation of ZnO micro-spheres can be used fabricate well-defined nanostructures in pure water without use of catalysts or additives. On the other hand, there are also some fundamental challenges: the control of the average size and the size distribution of nano-particles, the yield is relatively low compared that of conventional methods, *i.e.*. Thus, a further investigation should be focused on these unsolved drawbacks.

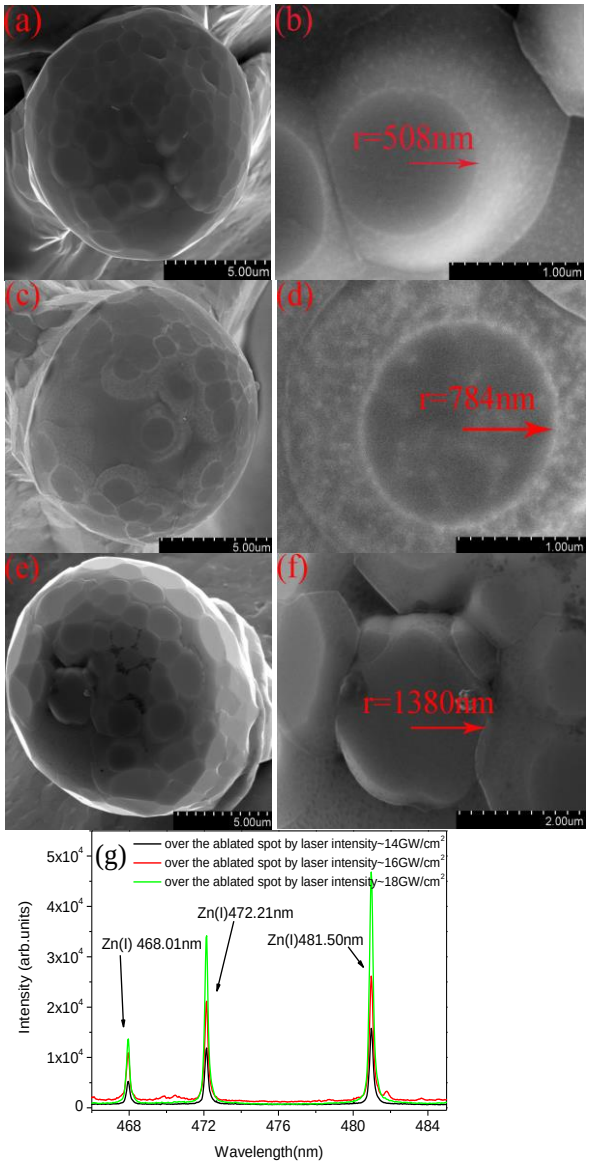

Fig. 4. (a-b, c-d, e-f) The typical SEM pictures (low and enlarged magnification, respectively) of individual ZnO micro-spheres fabricated by cumulative pulses laser etching at 14, 16 and 18 GW/cm^2, respectively. (g) The spatial distribution of representative spectral lines emitted from Zn atoms in the subsequent laser focused on the modified areas by cumulative pulses laser intensities at 14, 16 and 18 GW/cm^2, respectively.

4. Conclusion

In summary, we have demonstrated that well-defined ZnO hexagonal structures with sides about 30nm can be fabricated by pulsed laser (1064nm) fragmentation of ZnO micro-spheres (covered with polygonal facets) in pure water. The existence of surface roughness with amplitude less than the wavelength of the laser light plays an important or even dominating role in laser fragmentation process. The mechanism of laser fragmentation in water is likely to be dominated by physical other than chemical reaction in nature. Laser fragmentation or micro-etching of the facets on micro-spheres leads to the highly localized melting and evaporation. And the high temperature and pressure by laser induced evaporation should be responsible for the observed ZnO hexagonal crystal. Hopefully, the developed techniques will open a route toward functional nanostructure fabrication in the future.

Acknowledgments

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