UNIVERSITI PUTRA MALAYSIA

PREPARATION OF ZINC OXIDE NANOPARTICLES BY LASER ABLATION IN VARIOUS LIQUID MEDIA

RAHELEH JORFI

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By

RAHELEH JORFI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, In Fulfilment of the Requirements for the Degree of Master of Science

October 2014

DEDICATION

This thesis dedicated to
My father, my mother, my dear brother, and dear sister
for their love, endless support and encouragement with love

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

PREPARATION OF ZINC OXIDE NANOPARTICLES BY LASER ABLATION IN VARIOUS LIQUID MEDIA

By

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October 2014

Chairman: **Professor Azmi bin Zakaria, PhD**

Faculty: **Science**

A big challenge in the synthesis of nanoparticles (NPs) is particle agglomeration. This tendency can be inhibited by stabilization of NPs and therefore much effort by researchers has been undertaken to use different liquid media as stabilizers. In the present study we have investigated the fabrication of zinc oxide nanoparticles (ZnO-NPs) using Laser Ablation (LA) technique. The first objective is studying the effect of laser parameters on fabrication of ZnO-NPs and secondly investigating the medium effect on optical properties and size of ZnO-NPs. The LA to ZnO plate was carried out in various media such as distilled water, polyvinyl acetate aqueous solution, ethylene glycol, and rice bran oil, and then characterized by UV-vis, photoluminescence (PL), FT-IR spectroscopy, and TEM microscopy. It was revealed the generation of NPs by LA in various liquid media was higher in comparison with in distilled water. The increased NPs generation is attributable to solvent plasma confinement toward the plate. In addition, at longer ablation duration the size decrease of NPs was remarkable. The UV-vis absorption spectra of the ZnO-NPs are monitored to characterize the particle growth because the onset of absorption is associated with the particle size. It is observed that average NPs size decreases with the increase of ablation time. The decrement can be explained by the way that at longer ablation time, there is an increment of produced NPs from the plate since more interactions occurred between target and laser light. NPs with different sizes demonstrate different optical properties; when the particle diameter decreased there is a blue-shifted in absorption spectra. It can be observed that increasing repetition rate lead to larger particle diameter. This size increment is confirmed by the red-shifted absorption spectra. We analyzed PL spectra to see the emission spectra of fabricated NPs. Both the absorption and emission band positions are dependent on the polarity of the medium; in the medium the PL spectrum is much more sensitive than the absorption spectrum. PL spectra of all fabricated ZnO-NPs show two emission peaks; the first one is sharp and narrow UV emission corresponds to excitonic emission and the second one is broad blue-green emission commonly referred to a deep-level or a trap-state emission attributed to the singly ionized

oxygen vacancy of ZnO. TEM images also show the morphology of the ZnO-NPs as they were all spherical. The produced ZnO-NPs in rice bran oil were well dispersed; those fabricated in polyvinyl acetate were more stable than other liquid media. Ethylene glycol has ability to prevent agglomeration of NPs. The average diameter of the obtained ZnO-NPs in distilled water was large; 27.12 nm, on the other hand rice bran oil leads to fabricate fine ones; 14.17 nm.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia Sebagai memenuhi keperluan untuk ijazah Master Sains

PENEYEDIAAN NANOZARAH ZINK OKSIDA MELALUI ABLASI LASER DALAM PELBAGAI MEDIA CECAIR

Oleh

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Oktober 2014

Pengerusi: Professor Azmi bin Zakaria, PhD

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Cabaran utama dalam sintesis nano-zarah (NPs) adalah aglomerasi zarah. Kecenderongan ini boleh dihalang melalui penstabilan NPs dan oleh itu banyak usaha oleh penyelidik telah dilakukan menggunakan pelbagai media cecair sebagai penstabil. Dalam kajian ini kami telah menyelidiki fabrikasi nano-zarah zink oksida (ZnO-NPs) menggunakan teknik Ablasi Laser (LA). Objektif pertama adalah mengkaji kesan parameter-parameter laser dalam fabrikasi ZnO-NPs dan keduanya mengkaji kesan media cecair ke atas ciri optik dan ke atas saiz ZnO-NPs. LA ke atas plat ZnO telah dilakukan dalam pelbagai media seperti air suling, larutan cair polivinil asitat, etilena glikol, dan minyak dedak beras, dan kemudian dicirikan melalui spektroskopi-spektroskopi UV-vis, kefotopedarcahayaan, FT-IR, dan mikroskopi TEM. Adalah jelas bahawa penghasilan NPs melalui LA dalam pelbagai media cecair adalah lebih tinggi berbanding dengan yang di dalam air suling. Pertambahan penghasilan NPs adalah disabitkan dengan kurungan plasma pelarut kearah plat. Selain dari itu dalam tempoh ablasi lebih lama, pengecilan saiz NPs adalah luar biasa. Spektra penyerapan UV-vis dari ZnO-NPs adalah dimonitor untuk mencirikan pertumbuhan zarah kerana onset penyerapan adalaah dikaitkan dengan saiz zarah. Adalah diperhatikan bahawa purata saiz NPs mengurang dengan pertambahan masa ablasi. Pengurangan ini boleh dijelaskan melalui cara bahawa pada tempoh ablasi lebih lama, terdapat pertambahan NPs dihasilkan dari plat kerana lebih saling-tindak berlaku diantara target dan cahaya laser. NP dengan pelbagai saiz menunjukkan ciri-ciri optik berbeza; apabila diameter zarah mengecil akan terdapat anjakan biru dalam spektra penyerapan. Boleh diperhatikan bahawa penambahan kadar ulangan menjurus kepada diameter zarah lebih besar. Penambahan saiz ini disahkan oleh spektra penyerapan anjakan-merah. Kami menganalisa spektra PL untuk melihat spektra pancaran dari NPs terhasil. Kedua-dua kedudukan jalur penyerapan dan pancaran bergantung keatas kekutuban media; dalam media spektra PL adalah jauh lebih sensitif daripada spektra penyerapan. Spektra PL dari semua ZnO-NPs terfabrikasi menunjukkan dua puncak pancaran; yang pertama adalah tajam dan pancaran UV sempit bersabit dengan pancaran

eksotonik dan yang kedua adalah pancaran hijau lebar biasanya dirujukkan kepada paras-dalam atau suatu pancaran keadaan perangkap disabitkan kepada kekosongan oksigen terion tunggal dari ZnO. Imej TEM juga menunjukkan morfologi ZnO-NPs seolah mereka sfera semuanya. ZnO-NPs terhasil dalam minyak dedak beras adalah terserak secara sempurna; manakala yang difabrikasi dalam polivinil asitat adalah lebih stabil berbanding yang didalam medium cecair lain. Etilena glikol mempunyai kebolehan menghalang agglomerasi NPs. Daimeter ZnO-NPs yang diperolehi dalam air suling adalah paling besar, 27.12 nm; manakala yang didalam RBO adalah paling kecil, 14.17 nm.

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At the end of this step of my graduate period has allowed for a bit of reflection, and the many people who have contributed to both my work, and my life during of this period of time.

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Raheleh Jorfi

2014

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science**.** The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

LA	Laser ablation
NPs	Nanoparticles
DW	Distilled water
PVAc	Polyvinyl acetate
EG	Ethylene glycol
RR	Repetition rate
PL	Photoluminescence
FTIR	Fourier transform infrared
TEM	Transmission electron microscopy
Hz	Unit of frequency
nm	Nanometer
t	Time
λ	Wavelength
min	Minute

CHAPTER 1

INTRODUCTION

This chapter presents a brief introduction of the topic and concepts such as metal oxide nanoparticles (NPs), zinc oxide (ZnO) and pulsed laser ablation (PLA) used in this study. The statement of problems and objectives of the research is presented at the end of this chapter.

1.1 Introduction to Nanoscience

The word "nanoparticle" is normally used in the area of materials science to stand for particles in the size of less than 100 nanometres, which lie in the middle of the bulk state and the molecular state. However, similar physical and chemical properties of the bulk material can be seen in NPs larger than a few 10's of nanometres. Therefore, the maximum size limitation of nonoparticle that shows interesting properties different from those of the bulk is at almost 20 nanometers. The quantum size effect has been shown to emerge in NPs lying roughly in the range of 1-10 nanometers. As a result, as the size of a material is reduced down to nanoscale dimensions and more, its electronic properties alter significantly, whereby continuous energy bands of the bulk material changes to distinct energy levels of atoms (Barcikowski and Compagnini, 2013).

1.2 Metal Oxide Nanoparticle

In recent years, the fabrication and application of metal oxide NPs were greatly focused by researchers due to their distinctive physical properties which depend on variety of sizes, shape and the surrounding of NPs. In comparison, NPs are significantly different from those bulk materials as well as atomic or molecular structures. Since the NPs are sized between 100 to 1 nanometers, it exhibits large surface area and high percentage of surface atoms. Hence, when the size of materials approaches the nanoscale, the properties of materials also change and leading to the highest values of the activity to weight ratio (Jeng and Swanson, 2006).

Metal oxide NPs are receiving much more attention in physics, chemistry, and biotechnology. ZnO-NPs have numerous application, some of the more important applications are biosensors, antibacterial application and catalysis. Basically, the properties of nanostructured material related to the properties of NPs. Among them, the size and shape are the most prominent. Hence, the requirement in fabrication of metal oxide NPs is to develop the efficient method that ensured the stability and size controlled of metal NPs (Garcia and Rodriguez, 2007). They have also various optical properties. The nanoparticle optical spectrum depends on the particle morphology (size and shape), the nature of the metal, and the aggregation state of the particles. The optical properties and electronic structure of metal nanoparticle suspensions is mostly characterize by UV-Visible absorption spectroscopy, because of the relation between absorption bands and diameter of metal NPs.

1.3 Zinc Oxide

Advantages of ZnO are worth mentioning: It is a semiconductor that has a direct large band gap of 3.37 eV. The exciton binding energy of it is 60 meV that exceeds the room-temperature energy of 26 meV. The ZnO is a essential functional oxide that shows a transparent conductivity and exhibits near-ultraviolet emission. Due to its noncentral symmetry, ZnO is also a piezoelectric, that can be used to make transducers and electromechanical coupled sensors. ZnO is biocompatible and bio-safe material. Therefore, it can be utilized in many biomedical applications without need any covering (Garcia *et al.*, 2007).

These three exclusive characteristics of ZnO make it as the most imperative nanomaterials with many applications, in future research. The range of nanostructures which are offered here for ZnO, can open up lots of research fields in nanotechnology. Bulk ZnO is a wurtzite semiconductor with direct band gap which has the valence band with maximum separation by the spin-orbit interaction and crystal field.

ZnO-NPs were also widely examined as an emission material. This is due to the nanocrystallization that can improve the electrical and optical characteristics of wide-gap semiconductors which has a quantum confinement effect. However, impurity levels and surface defects are simply made during the nanoparticle fabricationprocess. The ZnO's lattice defects, like oxygen vacancies, are identified to make a green emission (Chen *et al.*, 2006). Many surface treatment methods, like annealing in oxygen, surface coating via polymeric materials, implanting in a silica matrix (Chakrabarti *et al.*, 2003), and also annealing face-to-face achieved in smother the green emission strength from ZnO nanostructures (Usui *et al.*, 2005).

1.4 Laser Ablation Technique

This study draws on the Laser ablation (LA) technique to prepare metal oxide NPs in liquids by ablating the metal palette with a high power, Nd:YAG pulsed laser. The resultant suspension of metal oxide NPs by LA is one of the common methods (Zamiri, 2010). Metal atoms, with a smaller amount of metal clusters are ablated from a plate during laser irradiation and are aggregated into sufficiently large sizes of metal oxide clusters. By changing the experimental condition of the ablation, the size distribution and concentration of these NPs can be readily controlled. The advantages of this method are the absence of chemical reagents or ions in the final preparation and the relative simplicity of the procedure (Amendola and Meneghetti, 2009).

This technique is a simple, straightforward and fast way for NPs generation and synthesis, in comparison with other techniques. It does not need a sustained reaction times, multi-step chemical synthetic procedures or high temperatures. It can also manufacture many different types of NPs from metallic to polymeric and semiconducting, as same as NPs of semiconducting alloys or compound multi-element metallic (Semaltianos, 2010).

It does not need the use of hazardous, toxic or pyrophoric chemical precursors to synthesis nanomaterial. Therefore, it is a laboratory safe, green and environmentally friendly method. In the occasion that production arises in fluid, the out coming NPs, colloidal solutions are ultrapure, and this assists the use of these NPs in biochemical or biological in vivo purposes (Wang and Herron, 1991).

The use of a powerful laser beam with a palette for material removing or ablation must be illustrated by relation between electron-phonon coupling time constant of the material and pulse width of the laser. The energy for the beam of laser is initially transferred to the material carriers. The free electrons are carriers in the case of metals and electrons of valence band which afterward stimulated to the conduction band are carriers in semiconductors. If the laser pulse width is larger than a nanosecond pulse, the energy of the beam remains to pass into the material even though carriers already have finished transferring their energy into the lattice. This causes the energy of laser to waste as heat, from the area where the beam of laser incident to the surface of material. In this case the material ablation even for low fluencies laser is through vaporization and melting, for example, a solid to vapour conversion (Zamiri *et al.*, 2011c).

Various sorts of pulsed lasers have been used for ablation. For example, ruby laser was amongst the foremost applied to ablate solid materials for chemical analysis purposes. Currently, most laser ablation experiments employ excimer lasers or Nd:YAG. Solid state Nd:YAG systems were commonly employed as they are moderately low-cost, need small repairs, and simply built into small commercial ablation systems. Moreover, excimer lasers use chambers filled by halogen gas preferred to solid-state crystals. The laser wavelength effects on ablation process. In most cases, the higher the ablation rate, the shorter the laser wavelength and lower the fractionation. In Nd:YAG lasers, the main wavelength is near infrared at the wavelength of 532 nm (Russo *et al.*, 2002).

1.5 Scope of Study

These days of full challenges to the research trend of synthesis and characterization of metal oxide NPs have led to many advantages and applications to the various field of industry. The demand of new technique in synthesis of metal oxide NPs has been developed to give pure and stable product of NPs.

Based on the objectives, the fundamental works to synthesize metal oxide NPs have been further investigated. The Q-switch Pulsed Nd:YAG laser is utilized to synthesize the ZnO- NPs with the frequency doubled wavelength (532 nm). The prepared ZnO-NPs were ablated in different liquid environment which are distilled water, polyvinyl acetate, ethylene glycol and rice bran oil. In this experiment, 10 ml of each solution is used. The ZnO target was ablated in different liquid at different times and different repetition rates to disperse ZnO-NPs. The different liquid environment are used to observe the stability of ZnO-NPs.

All of the solutions were characterized immediately after preparation for absorbance spectrum and distribution of size respectively. The different concentration of ZnO-NPs produced from laser ablates due to different ablation time. In addition, different particle size and size distribution of ZnO-NPs were obtained by different repetition rates. The significance is in the properties of NPs which are characterized by four different measurements which are UV-Visible Spectrometer, TEM, FTIR and PL.

1.6 Statement of Problem

Based on the reviewed literature, ZnO-NPs are often synthesized using chemical and physical methods that involves toxic chemical reagents, hazardous procedures or toxic and potentially harmful by-products. So, there is a Strong requirement for "green", economic, commercially possible as well as environmental friendly procedure for synthesis of ZnO-NPs as laser ablation method. On the other hand, lack of investigation about mpact of important factors (time, repetition rate, and media) on the ablation of ZnO-NPs. Therefore, a research gap for doing more investigation on effect of the medium on optical properties and size of ZnO-NPs is on demand. Before this, knowing the effect of laser parameters on fabrication of the new ZnO-NPs need to be found.

1.7 Objective of research

The present study aims to investigate the characteristics of ZnO-NPs produced from PLA from ZnO plate in the aqueous solutions and oil. Furthermore, it attempts to reveal the effects of surrounding molecules on size distribution and defect structure. The change of the liquid environment used in LA provides an easy and flexible method to modify NPs properties. More specifically the study pursues the following objectives:

1. To examine the effect of laser parameters as ablation duration, repetition rate on ZnO-NPs yield.
2. To investigate the medium effect on optical properties and size of ZnO-NPs.

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