ABSTRACT

ELECTROTHERMAL-VAPORIZATION-DEPOSITION FOR SYNTHESIS OF ZINC OXIDE NANOPARTICLES

An electrothermal vaporizer was designed and used for ZnO nanoparticle synthesis. Through this process the need for chemicals, catalysts, and expensive equipment has been minimized or eliminated. Further, by miniaturizing the process, the need for large sample material, long wait time and complicated multi-step synthesis has also been reduced or eliminated. ZnO nanoparticles were synthesized using the electrothermal vaporizer. Temperature was found to be a critical parameter for achieving synthesis of the particles. SEM images show three morphologies for the synthesized nanoparticles, namely, nanorods, nanobranches and nanowires. Through energy-dispersive x-ray spectroscopy the identity of the ZnO nanoparticles was confirmed.

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May 2013
ELECTROTHERMAL-VAPORIZATION-DEPOSITION FOR
SYNTHESIS OF ZINC OXIDE NANOPARTICLES

by

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APPROVED

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Zinc Oxide Nanoparticles</td>
<td>1</td>
</tr>
<tr>
<td>Applications of Zinc Oxide Nanoparticles</td>
<td>1</td>
</tr>
<tr>
<td>Zinc Oxide Nanoparticle Preparation Methods</td>
<td>5</td>
</tr>
<tr>
<td>System-Miniaturization of Nanoparticle Synthesis</td>
<td>19</td>
</tr>
<tr>
<td>System-Miniaturization of Zinc Oxide Nanoparticles Using Electro Thermal Vaporizer</td>
<td>20</td>
</tr>
<tr>
<td>RESEARCH GOAL</td>
<td>21</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>22</td>
</tr>
<tr>
<td>Electrothermal Vaporizer</td>
<td>22</td>
</tr>
<tr>
<td>Zinc Oxide Nanoparticle Synthesis</td>
<td>26</td>
</tr>
<tr>
<td>Sample Analysis</td>
<td>28</td>
</tr>
<tr>
<td>RESULTS</td>
<td>29</td>
</tr>
<tr>
<td>ZnO Nanoparticles</td>
<td>29</td>
</tr>
<tr>
<td>Elemental Analysis of Nanoparticles</td>
<td>33</td>
</tr>
<tr>
<td>CONCLUSION</td>
<td>36</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>37</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>41</td>
</tr>
<tr>
<td>APPENDIX A: PHOTOGRAPH OF ETV WITH GLASS COVER</td>
<td>42</td>
</tr>
<tr>
<td>APPENDIX B: PHOTOGRAPH OF POWER SUPPLY CONTROL CIRCUIT</td>
<td>44</td>
</tr>
<tr>
<td>APPENDIX C: PHOTOGRAPH OF POWER SUPPLY, CONTROL CIRCUIT AND SECONDARY POWER SUPPLY</td>
<td>46</td>
</tr>
</tbody>
</table>
APPENDIX D: PHOTOGRAPH OF HITACHI S-3500N SCANNING ELECTRON MICROSCOPE AT USDA AGRICULTURAL SCIENCE CENTER .........................................................................................................................48

APPENDIX E: PHOTOGRAPH OF GRAPHITE CUP ...............................................................................50

APPENDIX F: PHOTOGRAPH OF ZINC OXIDE NANOPARTICLES ON QUARTZ SLIDE .................................................................................................................................52
LIST OF FIGURES

Figure 1: Diagram of simple solution chemistry process for synthesizing ZnO nanoparticles employed by Baciskar et al. .......................................................... 7

Figure 2: SEM images of various ZnO morphologies synthesized by Baciskar et al. using simple solution chemistry ............................................................. 8

Figure 3: Diagram of simple solution-combustion method for ZnO nanoparticle synthesis employed by Ni et al. ............................................................ 9

Figure 4: SEM image of ZnO nanoparticles prepared by Ni et al. solution-combustion method .......................................................... 10

Figure 5: Diagram of Bechelany et al. polycarbonate membrane physical template assisted sol-gel method of ZnO nanoparticle synthesis. ....... 11

Figure 6: SEM images of close packed array of ZnO nanotubes synthesized by Bechelany et al. .......................................................... 12

Figure 7: Diagram of laser assisted catalytic growth method of ZnO nanoparticle synthesis by Son et al. .......................................................... 14

Figure 8: SEM images of various ZnO nanowires at different local sites in furnace synthesized by Son et al .................................................. 14

Figure 9: Diagram of ZnO synthesis method without catalyst and at low temperature developed by Liu et al. .................................................. 15

Figure 10: SEM image of ZnO nanowires produced without catalyst and at low temperature by Liu et al. .................................................. 16

Figure 11: Drawing of Yao et. al system for simple ZnO nanoparticle growth without the need for catalytic process .................................................. 17

Figure 12: SEM images showing the typical morphologies of the ZnO products produced by Yao et al.: (a) needle-like rods; (b) nanoribbons; (c) nanowires .................................................. 18

Figure 13: Schematic of the main chamber. The two power cables connect through the base and two a Teflon insulator to the stainless steel blocks. The blocks hold the graphite electrodes which hold between them a graphite cup. Coolant lines run through the base and supply water to the stainless steel blocks. A quarts slide is held up at an angle above the cup. A class cover seals the unit and is connected at the top to a vacuum pump and vacuum gauge .................................................. 23
Figure 14: Photograph of ETV shown from top with labels indicating position of primary components .......................................................... 24

Figure 15: Schematic of entire system. Vacuum pump removes air from chamber and Ar gas supplies inert atmosphere. Flow meter measures the flow of Ar gas and vacuum gauge reads pressure in the chamber. The power source supplies power to the workhead to heat the graphite cup. The control circuit adjusts the voltage and current to supply the proper power to the workhead. The multimeter measures voltage across a thermocouple which is converted into a temperature reading. Coolant lines allow water to circulate through workhead to prevent overheating.......................................................... 25

Figure 16: Photograph of main components of the entire system.......................... 26

Figure 17: Diagram of ETV base with substrate mounting bracket. Precise height of the substrate was key to growth of nanoparticles. Threaded stud with wing nuts give the ability to raise and lower the slide with great precision. The substrate is held in place by the two washers sandwiched between the two wing nuts.................................................. 27

Figure 18: SEM image of as prepared ZnO nanoparticle with nanorod morphology ............................................................................. 29

Figure 19: SEM image of ZnO nanoparticles showing the nanobranch morphology ........................................................................ 30

Figure 20: SEM close up image of ZnO nanoparticle with nanobranch morphology ......................................................................... 31

Figure 21: SEM image of ZnO nanowire stretching a great distance from the origin ................................................................. 32

Figure 22: SEM image of ZnO nanowire ........................................................................ 32

Figure 23: EDS spectrum showing identity of elements in sample: (a) position on sample where EDS was performed, (b)-(d) spectrum for the individual positions analyzed........................................................................ 35

Figure A1: Photograph of ETV with Glass Cover ................................................. 43

Figure B1: Photograph of Power Supply Control Circuit..................................... 45

Figure C1: Photograph of Power Supply, Control Circuit, and Secondary Power Supply ..................................................................... 47

Figure D1: Photograph of Hitachi S-3500N Scanning Electron Microscope at USDA Agricultural Science Center ................................................. 49

Figure E1: Photograph of Graphite Cup ................................................................ 51
Figure F1: Photograph of Zinc Oxide Nanoparticles on Quartz Slide

............... 53
INTRODUCTION

Nanoscience and Nanotechnology is quickly becoming one of the premier areas for study and discovery. Nanoscience involves the study of materials that range in size from 1 to 100 nanometers. Many times, structures of this size exhibit remarkable chemical, physical, and biological properties distinctive from conventional bulk material. For example, nanoparticles have a much greater surface area, and exhibit superior catalytic, electronic and photochemical properties.¹

Zinc Oxide Nanoparticles

ZnO is an important wide direct bandgap semiconductor (3.2 eV) with a large excitation binding energy of 60 meV and an absorption edge in the near-UV range². As a result, ZnO nanomaterials have attracted much interest for their potential applications in solar cell windows, varistors, optical waveguides, photodetectors, light-emitting devices, photonic crystals, gas sensors, piezoelectric transducers, and humidity sensors.

Applications of Zinc Oxide Nanoparticles

Solar Cell Applications

Wang et al. found that one-dimensional nanostructured zinc oxide semiconductors are especially suitable for n-type electrode material for solar cells. High transmittance in the visible wavelength region, a large surface area, high electron mobility along the growth direction and a highly efficient electron transport give ZnO nanostructures an advantage over other materials. Although ZnO is suitable for n-type electrodes, p-type electrodes must be replaced by other material due to the difficulty in the growth of p-type ZnO.³
Varistors

Varistors are well known electroceramic devices used for overvoltage protection in many electrical and electronic networks. Pillai et al. fabricated nano-ZnO varistors via solid state pyrolysis reaction of zinc acetate dihydrate and oxalic acid dihydrate at 500°C. These varistors show considerably higher breakdown voltage compared to those prepared by micrometric sized ZnO and commercial varistors.

Photodetectors

Ultraviolet (UV) photodetectors have a wide range of applications including flame sensing, environmental and biological research, astronomical studies, optical communication, and missile launch detection. UV photodetectors made from traditional materials exhibit limitations not limited to: the requirement for filters to block visible and infrared photons, degradation upon exposure to UV light of higher energy than the bandgap of the semiconductor and the need to be cooled to reduce dark current. ZnO has shown properties that allow for photodetectors with the ability to operate at high temperatures and in harsh environments. Jin et al. was able produce "visible-blind" UV photodetectors based on colloidal ZnO nanoparticles with high UV photocurrent efficiencies. Jun et al. developed photodetectors based on zero-dimensional ZnO nanoparticles which gave them better light absorption efficiency than other dimensional structures. Swanwick et al. reported on the first ZnO nanowire near-UV sensors that are insensitive to visible light and fabricated using a low temperature in situ process.

Light Emitting Devices

Two aspects of ZnO nanoparticles that make them attractive for light emitting devices are their resistance to detrimental oxidation and they do not
contain toxic materials. In optoelectronic devices a thin nanoparticle layer is embedded between two or more organic support layers. Neshataeva et al. found a method for low voltage ZnO nanoparticle light emitting device without the use of any organic support layers. The device, which operates at low voltages between 4 and 10 volts, is a preliminary step towards low-cost and convenient, printable nanoparticle luminescent devices.

Photonic Crystals

Demonstrating the versatility of ZnO nanoparticles, Redel et al. developed a method for preparing porous one-dimensional photonic crystals called Bragg mirrors (BM's) that have a tunable photonic stop band position based on nanoparticle size. With this method Redel was able to tune the properties on the nanoparticle films in terms of thickness, refractive index, porosity and surface area. This was done by controlling the alcohol solvent used in the synthesis. A roughly linear correlation was observed between the nanoparticle size and the film thickness, refractive index, and pore size, caused by the variation of reaction solvent. The nanoparticle size showed an inverse relationship to the refractive index of the thin films while pore size showed a directly proportional relationship to increasing particle size. The application of these photonic crystals range from heterogeneous catalysis, photocatalysis, and electrocatalysis to chemical sensors and solar cells.

Electronic Sensors

Fan et al. investigated the effects that oxygen adsorption has on the electrical behavior of ZnO nanowires and found that they can serve as potential building blocks for nanoscale electronic sensing devices. Due to the large surface-to-volume ratio of the nanowires detection sensitivity at appropriate gate
voltages is increased. The measurements demonstrate that ZnO nanowires have far better oxygen sensing performance than other traditional thin-film materials.

Piezoelectric Thin Films

One application for piezoelectric transducers that is gaining attention is strain monitoring, due to their ability to generate an electrical voltage drop when stressed. Traditionally, ceramic and polymer materials have been used as the material of choice however, not only can they be expensive but ceramic material tend to be brittle causing them to fail during operation, and polymers possess lower piezoelectricity and mechanical stiffness. Loh et al. discovered that they could overcome those issues by developing piezoelectric thin films made from ZnO nanoparticles. The advantages of ZnO for this application are high piezoelectricity, and mechanical properties that allow them to conform to structural surfaces while remaining stiff. The amount of ZnO embedded in the film was varied and the film’s stress-strain performance was tested for modules of elasticity, ultimate strength and ultimate failure strain. Loh found that increasing the ZnO weight fraction leads to a near-linear increase in their dynamic strain sensitivity and piezoelectricity. While 50-60% films were comparable to polymer and ceramic commercial films, in dynamic strain and piezoelectricity, they did not require high-voltage poling or mechanical stretching. It is possible that the properties of ZnO-based film will improve with increasing film thickness.

Humidity Sensors

One further application of ZnO nanoparticles is in humidity sensors that measure relative humidity in moisture-sensitive environments like humidors and clean rooms, detect moisture in many types of pure gases for semiconductor manufacturing and packaging, function in cryogenic process, and medical and
food science applications. Zhang et al. investigated ZnO nanorod and nanowire films for their humidity sensitive characteristics and demonstrated that ZnO films show promising application for humidity sensors. Zhang and company found that the resistance of the ZnO nanomaterial films decreased with increasing relative humidity and the resistance of ZnO nanowire samples change linearly with relative humidity. It was found that the sensitivity of the nanowire was greater than the nanorods due to the consistent morphology and size of the nanowires and the higher specific surface area. It was also shown that the nanomaterials present fast responses to the humidity pulse at relative humidity. Also noteworthy was the good long-term stability and high-humidity sensitivity.

**Zinc Oxide Nanoparticle Preparation Methods**

A myriad of methods for the preparation of ZnO nanoparticles have been developed including template-assisted growth, wet chemical synthesis, evaporative decomposition of solution, carbon thermal-reduction chemical vapor transport and condensation method, and nickel nitrate catalyst assisted growth method. These methods can be divided into two broad categories, namely wet methods and solid state methods. It may be helpful to include a third category of methods in which the synthesis process is miniaturized. There are benefits and drawbacks to each of the categories depending on desired outcome and application.

**Wet Methods**

Among wet methods, simple solution chemistry has shown merit in the number of different structures that have been synthesized. Low temperature hydrothermal growth allows for a vast array of substrates including glass and flexible polymers due to growth temperatures under 100°C. Sol-gel derived
nanocrystalline techniques are simple, inexpensive and produce more homogenous and smaller grain size\textsuperscript{14}.

**Simple solution chemistry.** Simple solution chemistry as a method for growing ZnO nanoparticles has some advantages over other solid state methods including simplicity, easy controllability, and cost effectiveness. Baciskar et al. used simple solution chemistry to synthesize a number of ZnO nanoforms including fibrous nanoflakes, nanobeads, nanoparticles, cactus, nanoneedles and hexagonal nanorods. Parameters such as deposition time, concentration of precursor solution, bath temperature, and pH of the bath were optimized in the experiment\textsuperscript{13}.

The ZnO films were synthesized directly over fluorine doped tin oxide (FTO) coated glass substrate. A precursor solution of zinc acetate dihydrate, hexamethylene-tetramine (HMTA) and 25\% ammonia was used as the deposition bath. After a pH of approximately 12.0 was achieved, the solution was stirred and transferred into a beaker containing cleaned FTO coated glass substrate placed at the bottom of the beaker. The bath was kept at room temperature for 40 h. After deposition, the substrate was removed, washed and dried in air. The as-deposited film, as is common with most wet methods, consisted of impurities such as zinc hydroxide. In order to remove these impurities the films were annealed at 100-200\degree C for 1 h (see Figure 1). In order to synthesize the various shapes mentioned above, some changes were made to the chemical process. For example: the ratio of zinc acetate dihydtrate and HMTA was changed; a different precursor, namely ammonium zincate complex and hot mil-Q-water were used; the ZnO films were grown on seeded FTO substrates using the successive ionic layer adsorption and
reaction (SILAR) method. Depending on the method used, annealing times were varied according to the amount of impurity in the sample.

Figure 1: Diagram of simple solution chemistry process for synthesizing ZnO nanoparticles employed by Baciskar et al.

Wettability tests were performed on the films which show the contact angle between the liquid and solid film. From this angle the hydrophobic or hydrophilic nature of the film can be determined. The annealed ZnO film deposited by SILAR and FTO coated samples had contact angles that demonstrate they hydrophilic nature of the ZnO nanoparticles. Analysis of the product showed a number of morphologies for the annealed ZnO films. The morphologies consisted of flower like structures, nanobeads and fibrous interconnected flakes (see Figure 2).

Simple solution chemistry has been employed to successfully grow ZnO nanostructures on FTO coated glass in aqueous medium. However, a great deal of time is required in the growth of the nanomaterial. In some cases 40 h or more is needed to complete the reaction. Also, while this method is touted as being performed at room temperature, it is important to note that in order to remove
Figure 2: SEM images of various ZnO morphologies synthesized by Baciskar et al. using simple solution chemistry.
impurities, the sample must be annealed in some cases to 200°C which not only adds to the complexity of the method but also to the time required.

**Simple solution combustion method.** Although many solution methods for preparing ZnO nanoparticles have been developed there is still a need to search for more simple and inexpensive methods that produce high yields. Ni et al. came up with a process that has many advantages. It doesn't require any complex equipment and is therefore cheap and simple. It is environmentally friendly since the only byproducts are carbon dioxide and water. The reaction is safe and quick and the yield is above 95%.

The experiment was performed by dissolving zinc acetoxy in 100 ml of 60/40 ethanol/ethyleneglycol solution. The solution was then transferred into a spirit lamp by cotton lampwick and the lamp was fired. A yellow substance appeared on the lampwick and when extinguished turned white. The white product was repeatedly washed with distilled water and ultrasonic and centrifugal treatments. It was then dried at 50°C for 5 h (see Figure 3).

![Diagram of simple solution-combustion method for ZnO nanoparticle synthesis](image)

**Figure 3:** Diagram of simple solution-combustion method for ZnO nanoparticle synthesis employed by Ni et al.
The product was analyzed by a number of methods including powder x-ray diffraction (XRD), transition electron microscopy (TEM) and scanning electron microscopy (SEM) imaging (see Figure 4), and ultraviolet ultraviolet-visible spectroscopy (UV-vis). The XRD pattern indicated that the product was hexagonal ZnO in the wurtzite structure and had good crystallinity defined by strong and narrow diffraction peaks. The TEM and SEM images showed that the product was nearly spherical nanoparticles with a mean diameter of 80 nm. The UV-vis absorption spectrum showed an absorption peak centered at 374 nm while two emission peaks were centered at 391.5 and 499.5 nm\textsuperscript{15}. It is interesting to note that although preparing ZnO nanoparticles using low temperature hydrothermal growth claims to be a quick method, it nonetheless requires an excess of 5 h to produce the final product.

![Figure 4: SEM image of ZnO nanoparticles prepare by Ni et al. solution-combustion method](image)

**Sol-gel methods.** Sol-gel derived ZnO nanoparticle growth has shown interest due to its simplicity and the ability to grow nanotubes. However, the quality of the structures in terms of morphology tends to be very low and because of the need for a membrane, the elimination of the membrane is difficult without
deterioration of the nanotubes. Bechelany et al. improved upon the sol-gel method by using polycarbonate membranes assisted by physical templating which also allowed control over the size of the nanotubes produced.

In a typical synthesis, zinc nitrate hydrate was dissolved in deionized water and mixed with urea CO(NH$_2$)$_2$ to form a molar ratio of 1:80. A polycarbonate membrane with random distribution of nanometric pores was added to the solution and fixed to the bottom of the reaction vessel. The vessel was immersed in ultrasonic bath for 1 h at room temperature. The temperature was raised to 80°C for 24 h. A white precipitate formed on the membrane which was removed, put into a furnace and annealed at 150°C for 1 h then 600°C for another 10 h. After heating, a cooling period of approximately 4 h is required (see Figure 5). The annealing process eliminates the polycarbonate membrane and facilitates the crystallization of the ZnO nanoparticles.

![Diagram of Bechelany et al. polycarbonate membrane physical template assisted sol-gel method of ZnO nanoparticle synthesis.](image)

Analysis of the product revealed only Zn and O peaks. Absence of a carbon peak confirm that the polycarbonate membrane used as a template was completely eliminated during the annealing process. The product consisted of
close-packed 1D, hollow nanostructures of 20 µm in length and 200 nm in diameter (see Figure 6). The nanotube wall is formed of agglomerated ZnO nanoparticles that are homogeneous and have a diameter smaller than 10 nm\textsuperscript{1b}.

![Figure 6: SEM images of close packed array of ZnO nanotubes synthesized by Bechelany et al.](image)

Although the sol-gel method is appropriate for the synthesis of nanotube shaped particles it is limited in other morphologies such as nanowires and nanospheres. Also, because of the annealing process, a tube furnace is needed which adds to the expense of the method. The time needed to carry out the synthesis is in excess of 30 h.

**Solid State Methods**

Solid state methods of ZnO nanoparticle synthesis have many advantages including no drying time requirement, little or no impurities and therefore no need for annealing, and depending on the method, more control over the morphologies
of the crystals. Laser assisted catalytic growth has proved successful in synthesizing well aligned ZnO nanowires on Au coated Al$_2$O$_3$ substrates$^{16}$. Catalyst free ZnO nanomaterial synthesis eliminates the possibility of harmful effects caused by the catalyst and keeps growth temperature under 600 °C. Simple thermal evaporation provides a method for synthesizing crystalline ZnO nanowires and nanoribbons without the need for neither tedious catalytic processes nor carrying gas.

**Laser assisted catalytic growth method.** Laser assisted catalytic growth was achieved by Son et al. The use of a laser to aid in ablation of the sample facilitates nanoparticle growth. Au thin film was coated on Al$_2$O$_3$ substrate by thermal evaporation. Multiple substrates were placed at distances of 1, 3, 5, and 7 cm which relate to the different temperature of synthesis. A ZnO ceramic target in an alumina tube was placed in a furnace and irradiated by a focused Nd:YAG laser (355 nm). The lower wavelength laser has an energy density of 3 J/cm$^2$ in the furnace. Ar gas was introduced into the system at a flow rate of 50 sccm and the pressure was maintained at 1 Torr. The temperature of the furnace was ramped up to 950 °C at a rate of 50 °C per min and kept at that temperature for 30 min (see Figure 7).

The diameter and length of the ZnO nanowires varied with substrate position. Diameters ranged from 120-200 nm. The average length was greater than 2 µm (see Figure 8). The photoluminescence spectra (PL) indicate that green emission related to defects in ZnO was nearly not observed$^{16}$. While this method is a relatively simple and general method for the production of ZnO nanoparticles, it still requires the use of expensive equipment and substrate preparation.
Figure 7: Diagram of laser assisted catalytic growth method of ZnO nanoparticle synthesis by Son et al.

Figure 8: SEM images of various ZnO nanowires at different local site in furnace synthesized by Son et al.
**Low temperature method.** Many of the solid state methods of ZnO nanoparticle synthesis require a catalyst and high temperatures ranging from 800-1100°C. Presence of a chemical catalyst can in many instances be harmful to its applications in nanodevices and high-temperature growth techniques limit fabrication of ZnO nanomaterials in gentle circumstances. Liu et al. fabricated well aligned ZnO nanorods and nanowires without a catalyst and at a low temperature of about 550°C\(^\text{17}\).

The substrate was prepared by electrochemical etching of Si wafers in a mixture of hydrofluoric acid, distilled water and ethanol. A current density of 10 mA/cm\(^2\) was applied to the mixture for 10-30 min. Zn powders, as the source materials, were placed in a quartz vessel and inserted in a single-stage furnace. Furnace temperature was raised to 550°C and then oxygen gas was fed into the system. The oxygen flow rate was regulated at 10 and 20 sccm and the argon flow rate was held constant at 200 sccm (see Figure 9). After 30 min a white fluffy material formed on the silicon surface.

![Figure 9: Diagram of ZnO synthesis method without catalyst and at low temperature developed by Liu et al.](image-url)
ZnO nanowires of high density and a uniform diameter of about 40 nm and length of 2 µm were synthesized on the substrate (see Figure 10). By varying the ratio of flow rates of argon to oxygen gas, high density nanorods were also grown at 550ºC. The nanorods had a similar length to that of the nanowires with a diameter of 90 nm. Although no catalyst was used, some attention must be given to the preparation of the substrate. Also, as with most of the solid state methods, the use of a tube furnace is required.

Figure 10: SEM image of ZnO nanowires produced without catalyst and at low temperature by Liu et al.

Catalyst free method. Yao et al. developed a simple method for developing ZnO nanoparticles that does not involve the use of a tedious catalytic process nor carrying gas. The synthesis process was done in a quartz tube of 1 cm in diameter and 20 cm in length. The source material, ZnO powder, was placed in the closed end of the quartz tube and placed in a horizontal tube furnace and heated to 1100 ºC for approximately 30 min. The quartz tube was then drawn out and allowed to
cool to room temperature. White product formed on the inner wall of the quartz tube in the temperature range of 800 to 500 ºC (see Figure 11).

![Diagram of Yao et. al system for simple ZnO nanoparticle growth without the need for catalytic process.](image)

Figure 11: Drawing of Yao et. al system for simple ZnO nanoparticle growth without the need for catalytic process.

SEM images of the white product revealed three morphologies for the ZnO nanostructures: needle-like rods, nanoribbons and nanowires (see Figure 12). The needle-like rods were formed in the region where growth temperature was about 800-750 ºC. The nanoribbons were found in region II which had a growth temperature of 750-650 ºC. ZnO nanowires grew mainly at a temperature range of 650 to 500 ºC. The diameter of these structures varied greatly, ranging anywhere from 10 to 200 nm\(^{18}\).

This method has the benefit of not needing any complicated catalytic processes. It also doesn't require condition of low pressure and therefore no vacuum pump is required. However, due to the large quartz tube a substantial sample volume must be used as well as the use of a tube furnace.
Figure 12: SEM images showing the typical morphologies of the ZnO products produced by Yao et al.: (a) needle-like rods; (b) nanoribbons; (c) nanowires.
System-Miniaturization of Nanoparticle Synthesis

There have been a few attempts to miniaturize the synthesis of nanoparticles. Miniaturizing the process shows promise in overcoming difficulties in controlling the shape, size and purity of nanoparticles in a safe and cost-effective manner. The majority of these attempts have been carried out in microstructure reactors.

Jain et al. used micro reaction technology to synthesize ceramic nanoparticles. In terms of design, alumina was used as the microreactor which is capable of working at high temperature. The design also lowered fabrication cost by decreasing the number of plates typically needed by about 3 fold. A major drawback of this method, however, is that it is only appropriate for non-oxide ceramic nanoparticle synthesis.

Sue et al. were able to synthesize zinc oxide nanocrystals using a microreactor. Solutions were prepared by using precise amounts of ZnSO₄ and KOH in distilled water. The solutions were then fed through an experimental flow apparatus made up of 0.59 mm i.d. stainless steel tubing by two pumps. The reactor temperature was controlled by an electric furnace and the fluid was cooled at the exit of the reactor by quenching with cold water. The crystals were collected by filtering the slurry solution and dried at 60°C for 1 day. The collected crystals were analyzed for size and elemental make-up. They were found to be ZnO nanocrystals that ranged in size from 10 to 100 nm. Although this method was successful in synthesizing ZnO nanocrystals, it is a very tedious method that requires a full day for drying time and has many of the drawbacks of the other aforementioned wet methods for ZnO synthesis.
System-Miniaturization of Zinc Oxide Nanoparticles
Using Electro Thermal Vaporizer

Reviewed methods for the synthesis of ZnO nanoparticles include so called wet methods and solid state methods. Wet methods have the advantage of simplicity in terms of required equipment and relative low cost of production. Most methods are carried out at room or low temperature. However, they tend to be time consuming as they require reaction, mixing or sonication and drying times of hours and even days. They may also introduce impurities into the product which require an annealing process which adds to the time and tediousness of the procedure. Solid state methods generally take less time but often require complicated and expensive catalyst preparation. Even those methods that have eliminated the need for a catalyst, require the use of expensive equipment like tube furnace and vacuum chambers. Due to the scope of the equipment involved, all of the methods currently being used require a relatively large amount of sample. Miniaturizing the process can help eliminate some of the drawbacks, as well as improve the ability to control the size, shape and purity of the nanoparticles.

In this work a truly simple, inexpensive, efficient and miniaturized method for ZnO nanoparticle synthesis is developed. No catalyst is needed and therefore no complicated, time consuming or expensive substrate preparation is required. Total time to synthesize nanoparticles is less than 10 min. An electrothermal vaporizor (ETV) is used for heating of the sample which is an economical substitution for a tube furnace. There is no use of any other expensive equipment. Because of the miniaturization of the process, an extremely small amount of sample is all that is needed to grow the ZnO nanoparticles. In addition, heat transfer and other parameters can be precisely controlled.
RESEARCH GOAL

The purpose of this work is to employ an electrothermal vaporizer (ETV) for the synthesis of nano-sized structures. Secondly, the ETV is used to synthesize zinc oxide nanoparticles.

In order to achieve ZnO synthesis, the ETV must be given an appropriate cover that will allow for the attachment of vacuum and vacuum gauge lines. A thermocouple that will allow for the temperature measurement of the sample must be designed and incorporated. An appropriately sized graphite "cup" to house the sample must be designed and fabricated. The chamber must house two stainless steel blocks which hold the electrodes and the cup. Cooling lines must be attached to keep the blocks cool and power cables must attach to the two blocks housed inside the chamber. The chamber must be built air tight so that proper vacuum can be maintained. A power source to heat the cup and an electric circuit to control the power source must be designed and assembled. A bracket to hold the inverted collection substrate must also be designed and fabricated.

It is already known that ZnO nanoparticles can be synthesized using large tube furnaces, in solution, and by using microreactor technology. What is not known is if ZnO nanoparticles can be synthesized using an incredibly simple and inexpensive electrothermal vaporizing chamber with small graphite cup. The product will be analyzed for size, shape, purity and elemental makeup.
EXPERIMENTAL

Electrothermal Vaporizer

The ETV chosen is a laboratory built unit originally designed for sample atomization for atomic spectroscopy (components shown in Appendices A-E). The workhead is composed of two stainless steel blocks separated by 3.00 cm. Each block has been machined to accept a 4.0 mm o.d. graphite rod. The graphite rods are held firmly in place by applying a clamping pressure with machine screws. The blocks have also had cooling channels drilled in them to allow water to circulate and cool the blocks during operation. The blocks are mounted on a cylindrical aluminum platform and attached using threaded studs that extend from the bottom of the blocks and through two holes drilled in the base. These threaded studs not only allow for the securing of the blocks to the base but also allow attachment of the electrical cables that supply the current to the graphite cup (see Appendix E). Two thin Teflon squares insulate the blocks from the platform. Teflon cooling lines with an i.d. of 3/32” were attached to the cooling holes drilled into the blocks and routed out through the bottom of the aluminum platform. There is a hole located in the middle of the aluminum platform which has the gas line attached for gas introduction. Two small holes in the base allow thermocouple leads to extend inside the chamber. The aluminum platform has a lip machined into the outside edge which accepts a 3.5” diameter o-ring. The o-ring and lip create an air tight seal with the cover which was made by blown glass. The cover fits snugly on the base and has a conical shape at the top with two outlets made for attaching the vacuum pump and the vacuum gauge. A graphite cup 6.0 mm tall and 6.0 mm o.d. was made and "sandwiched" between two graphite rods inserted into the two blocks and positioned in the middle, between the blocks and
directly above the gas flow. A bracket was made to hold the substrate at an angle above the cup (see Figures 13, 14 and Appendix A, B). It was made from a 2.5" long by 7/32" diameter threaded stud which was screwed into the base 2.5 cm behind the cup. It was fitted with two washers and two wingnuts in such a way that the wingnuts and washers clamp onto the substrate and hold it at an angle above the graphite cup. The clamp has the ability to adjust the height of the substrate above the cup by screwing the wingnuts up or down.

Figure 13: Schematic of the main chamber. The two power cables connect through the base and two a Teflon insulator to the stainless steel blocks. The blocks hold the graphite electrodes which hold between them a graphite cup. Coolant lines run through the base and supply water to the stainless steel blocks. A quarts slide is held up at an angle above the cup. A class cover seals the unit and is connected at the top to a vacuum pump and vacuum gauge.
Compressed argon gas of high purity is introduced into the system through the hole in the bottom of the base. The flow-rate is controlled by an in line adjustable valve. An Alltech digital flow meter is placed in line to measure the gas flow rate.

Vacuum is achieved by attaching a Welch Scientific Duo Seal vacuum pump model 1402 to the top of the glass chamber cover. Pressure in the chamber is measured by attaching a Hastings Vacuum gauge model VT-6B to the chamber as well. To achieve the desired vacuum, care must be taken to ensure that all vacuum lines and gas lines are securely attached. Any small leak will make it impossible to decrease the pressure to the proper value.
The temperature of the graphite cup is monitored using a tungsten/rhenium thermocouple from Omega. The thermocouple is connected to a Fluke model 8800A multimeter for voltage measurement. Voltage is recorded and converted into temperature using a revised thermocouple reference table.

The power source for heating the graphite cup was constructed from five commercially available computer power supplies. Each power supply is rated up to 300 W maximum power. A circuit was constructed to control the power output of the power source. A Heath Zenith Tri-Power supply was used in conjunction with the main power supply in order to provide constant voltage to the circuit (see Figures 15, 16 and Appendix C).

Figure 15: Schematic of entire system. Vacuum pump removes air from chamber and Ar gas supplies inert atmosphere. Flow meter measures the flow of Ar gas and vacuum gauge reads pressure in the chamber. The power source supplies power to the workhead to heat the graphite cup. The control circuit adjusts the voltage and current to supply the proper power to the workhead. The multimeter measures voltage across a thermocouple which is converted into a temperature reading. Coolant lines allow water to circulate through workhead to prevent overheating.
Zinc Oxide Nanoparticle Synthesis

Substrate Preparation

The substrate chosen for ZnO nanoparticle growth was a Chemglass 50 x 25 mm quartz slide, part #CGQ-0640-02. Quartz was used as an alternative to glass slides due to its higher melting point and greater structural integrity. Unlike other methods, the slides were left undoped and free of any films or other treatments. The quartz slides were prepared by first washing with a 1M Nitric Acid solution. After washing, the slides were rinsed once with acetone followed by a final rinsing with deionized water.
ETV Operation and Procedure

ZnO nanoparticles were grown from ZnO powder. J.T. Baker ZnO powder, reagent #4358-1 was used. A very small portion of ZnO powder, less than the tip of a pencil lead, is loaded into the graphite cup. Any excess powder that may have fallen onto the workhead base is removed. A quartz slide is inserted into the slide holder which is adjusted to a height of approximately one centimeter above the cup (see Fig. 17). The correct height of the slide is imperative to nanoparticle growth. If the slide is too high, no product is found on the slide after operation. Conversely, if the slide is too close to the cup the product collected will be clumps of ZnO instead of nanoparticles. There seemed to be no specific height that always produced good results, but trial and error was employed until synthesis was achieved.

Figure 17: Diagram of ETV base with substrate mounting bracket. Precise height of the substrate was key to growth of nanoparticles. Threaded stud with wing nuts give the ability to raise and lower the slide with great precision. The substrate is held in place by the two washers sandwiched between the two wing nuts.
The glass cover was placed on the unit and the vacuum pump turned on. Once the vacuum pump was running argon gas was introduced into the system until the chamber was purged of all air. The gas valve was closed down to achieve a flow rate of 17 sccm. At this flow rate the pressure in the system was ~1 Torr. Subsequently, the cup was ramped quickly to a temperature that ranged from 700-800 °C and held at a constant temperature for 1 min. Immediately after heating a white film could be seen forming on the bottom side of the slide. It is important to note that this temperature is the outside temperature of the graphite cup as the thermocouple was only pressed up against the side of the cup by its own spring action. During heating a white substance formed on the bottom of the substrate (see Appendix F). After heating, the power to the cup was shut off and the product was left to cool for 5 min. The vacuum pump and gas flow were shut off and the slide removed and placed in a vacuum desiccator for storage and transport.

**Sample Analysis**

The Sample was first viewed using a dark field light microscope with a total magnification of 1000X. This step was necessary to confirm the presence of micro or nano sized particles. If nano sized particles were suspected to be present, slides were analyzed using a SEM (see Appendix D). Elemental analysis on the product was performed by energy-dispersive x-ray spectroscopy (EDS) to confirm the identity of the nanoparticles formed.
RESULTS

ZnO Nanoparticles

ZnO nanoparticles were grown in the electrothermal vaporizer. SEM images show three distinct morphologies for the as prepared nanostructures: nanorods, nanobranches and nanowires. Figure 18 shows the morphology of the nanorods. These were the shortest of the three morphologies with an average length of approximately 1.5 μm. The diameter of the nanorods was very consistent compared to the other morphologies and averaged about 200 nm. The hexagonal shape of the nanorods is evident and is consistent with the wurtzite structure commonly reported in the literature. More nanorod shaped particles were formed than nanobranches or nanowire.

Figure 18: SEM image of as prepared ZnO nanoparticle with nanorod morphology
The second morphology is shown in figures 19 and 20. These are referred to here as nanobranches for their resemblance to the branches on a tree. The length and diameter of the nanobrach morphology is very diverse. They range in length from more than 10 um. down to tiny off shoots from other branches that are less than 10 nm. The diameters of the nanobranches range from 20 to 200 nm. The cause of the branching is due to various chamber conditions. Variations in temperature, pressure and flow rate of the argon gas may have caused the inconsistent growth pattern and resulted in the off shoots and angles seen in the nanobranches. Although this morphology is not typically a desirable one it may have some potential application and warrant further study. If the branching could be controlled during synthesis nanocircuits could be built to control the electronics in nanomachines.

Figure 19: SEM image of ZnO nanoparticles showing the nanobranch morphology.
The third type of morphology shown in figures 21 and 22 is nanowire. The nanowire was the least common of the three morphologies seen. There were however, some very long stretches of nanowire that seemed to bridge from one cluster of particles to another. The nanowire had a diameter that ranged from 100 to 200 nm and ranged in length from about 5 um to 25 um.

In most solid state methods for preparing ZnO nanoparticles, position of the substrate from the heat source produces nanoparticles of different morphology, according to the temperature at which they are grown\textsuperscript{18}. Placing three substrates at three different positions in a tube furnace would produce multiple morphologies on the three different slides. In this data we see three different morphologies appearing on the same substrate indicating that the temperature is either fluctuating during growth or there are micro temperature zones where different morphologies grow according to the temperature of the zone they are in. In either case we can see further evidence that temperature plays an important role in what morphology will form when growing ZnO nanoparticles.

Figure 20: SEM close up image of ZnO nanoparticle with nanobranch morphology.
Figure 21: SEM image of ZnO nanowire stretching a great distance from the origin.

Figure 22: SEM image of ZnO nanowire
Elemental Analysis of Nanoparticles

Elemental analysis of the product was done by EDS. The resolution of the EDS beam is not small enough to zoom in on the nanoparticles, however, it does reveal the elements present in the various regions where the nanoparticles were found. Figure 23 shows the spectrum for five different substrate locations where EDS was performed. All five spectrums indicate the presence of zinc atoms and oxygen atoms. There is also a small peak indicating the presence of carbon atoms. This is due to some ablation of the graphite cup during heating.

Points 1-4 show almost identical peaks. At 0 keV there is a small peak for carbon then a larger peak for oxygen and the largest peak being that of zinc. The close proximity of these peaks indicate the ZnO structure. There is a second and third peak for zinc at 10 keV indicating the presence of individual zinc atoms. Point 5 however, has a dissimilar spectrum. This is consistent with the location of point 5 being outside of the area where the bulk of the ZnO nanoparticles appear to be present. In this region the peak for ZnO and carbon is much smaller while the largest peak is in the location of the zinc atom.
Figure 23: EDS spectrum showing identity of elements in sample: (a) position on sample where EDS was performed, (b)-(d) spectrum for the individual positions analyzed.
CONCLUSION

The ETV was successfully employed to grow nanoparticles. Gas flow, pressure, temperature and stage height were all components that could be controlled for nanoparticle synthesis.

Nanometric ZnO particles were successfully synthesized through a novel, miniaturized solid state method. EDS results showed that ZnO was present in the region where nanoparticles were found. SEM imaging showed that there were three different morphologies for the ZnO nanoparticles synthesized. The majority of the particles were nanorod and a number of nanobranches were also observed. Although less frequent, nanowires were also successfully grown. The particles obtained had a range of diameters anywhere from 10 to 200 nm.

The method has many advantages over others currently in use. The process is single step and catalyst free which eliminates the need for complicated multistep procedures. It is a solid state method which eliminates the need for messy solution based chemistry that often introduces impurities in the product. No expensive equipment is needed and is therefore a very economical way to produce nanoparticles. The method is miniaturized so that nanoparticles can be synthesized from a very small sample and the whole process takes less than 10 min. It is desirable that further work be done to optimize the experimental conditions in order to synthesize particular nanostructures using this method.
REFERENCES
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APPENDIX A: PHOTOGRAPH OF ETV WITH GLASS COVER
Figure A1: Photograph of ETV with Glass Cover
APPENDIX B: PHOTOGRAPH OF POWER SUPPLY CONTROL CIRCUIT
Figure B1: Photograph of Power Supply Control Circuit
APPENDIX C: PHOTOGRAPH OF POWER SUPPLY, CONTROL CIRCUIT AND SECONDARY POWER SUPPLY
Figure C1: Photograph of Power Supply, Control Circuit, and Secondary Power Supply
APPENDIX D: PHOTOGRAPH OF HITACHI S-3500N SCANNING ELECTRON MICROSCOPE AT USDA AGRICULTURAL SCIENCE CENTER
Figure D1: Photograph of Hitachi S-3500N Scanning Electron Microscope at USDA Agricultural Science Center
APPENDIX E: PHOTOGRAPH OF GRAPHITE CUP
Figure E1: Photograph of Graphite Cup
APPENDIX F: PHOTOGRAPH OF ZINC OXIDE NANOPARTICLES ON QUARTZ SLIDE
Figure F1: Photograph of Zinc Oxide Nanoparticles on Quartz Slide
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