

2020-01-01

SynThesis and Characterization Of Material Systems for 3D Printed Smart Structures

Hilda Fontes
University of Texas at El Paso

Follow this and additional works at: https://scholarworks.utep.edu/open_etd



Part of the [Materials Science and Engineering Commons](#), and the [Mechanics of Materials Commons](#)

Recommended Citation

Fontes, Hilda, "SynThesis and Characterization Of Material Systems for 3D Printed Smart Structures" (2020). *Open Access Theses & Dissertations*. 2965.
https://scholarworks.utep.edu/open_etd/2965

This is brought to you for free and open access by ScholarWorks@UTEP. It has been accepted for inclusion in Open Access Theses & Dissertations by an authorized administrator of ScholarWorks@UTEP. For more information, please contact lweber@utep.edu.

SYNTHESIS AND CHARACTERIZATION OF MATERIAL SYSTEMS
FOR 3D PRINTED SMART STRUCTURES

HILDA FONTES

Master's Program in Mechanical Engineering

APPROVED:

Yirong Lin, Ph.D., Chair

Tzu-Liang (Bill) Tseng, Ph.D.

David Espalin, Ph.D.

Stephen L. Crites, Jr., Ph.D.
Dean of the Graduate School

Copyright ©

by

Hilda Fontes

2020

SYNTHESIS AND CHARACTERIZATION OF MATERIAL SYSTEMS
FOR 3D PRINTED SMART STRUCTURES

by

HILDA FONTES, B.S.

THESIS

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE

Mechanical Engineering Department

THE UNIVERSITY OF TEXAS AT EL PASO

May 2020

ACKNOWLEDGEMENTS

I would like to acknowledge everyone who helped me to accomplish this goal. Especially my parents, siblings, life partner, and friends. Thank you for all your support, love, and motivation.

I also want to express my endless gratitude to my advisor and committee members. This achievement couldn't be possible without your guidance and support.

ABSTRACT

The silica hollow spheres have demonstrated excellent results in multiple applications such as light-weight composites, and optical applications as a glass coating. This material also exhibits excellent thermal, shock impact, and hydrophilic properties extremely useful for industrial applications. However, a controllable size of the particle is desired to further increase the number of applications of the silica hollow spheres.

This thesis aims a method to fabricate silica hollow spheres in a single step with a controlled diameter size. A study was developed to demonstrate the particle size change when adjusting the molecular weight of the medium by using different alcohol solvents. A 70% and 58% size increase in the PS core and hollow sphere, respectively, were successfully obtained during this research work.

The fabricated silica hollow spheres are expected to be used as a photovoltaic cell coating due to their hydrophilic behavior. The material is expected to be easily printed via paste extrusion and exhibit high resistant mechanical and thermal properties.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	iv
ABSTRACT.....	v
TABLE OF CONTENTS.....	vi
LIST OF TABLES.....	viii
LIST OF FIGURES.....	ix
CHAPTER 1: INTRODUCTION.....	1
RESEARCH MOTIVATION.....	1
POWER GENERATION FROM RENEWABLE ENERGY SOURCES.....	2
SOLAR ENERGY.....	3
MANUFACTURING OF SOLAR CELLS.....	4
EFFECT OF HUMIDITY ON SOLAR CELL PERFORMANCE.....	4
SUPER-HYDROPHILIC COATING.....	5
SILICA HOLLOW SPHERES.....	6
PROPERTIES OF SILICA HOLLOW SPHERES.....	6
APPLICATIONS OF SILICA HOLLOW SPHERES.....	7
CHAPTER 2: FABRICATION OF SILICA HOLLOW SPHERES.....	8
INTRODUCTION.....	8
POLYSTYRENE PARTICLE PREPARATION.....	9
DISPERSION POLYMERIZATION.....	9
EXPERIMENTAL PROCEDURE.....	10
HYDROLYSIS AND CONDENSATION OF TEOS.....	10
EFFECT OF TEOS CONCENTRATION ON SILICA HOLLOW SPHERES.....	11

POLYSTYRENE PARTICLE DISSOLUTION.....	12
EFFECT OF AMMONIA CONCENTRATION ON SILICA HOLLOW SPHERES.....	12
CHAPTER 3: RESULTS.....	14
INTRODUCTION	14
SIZE INCREASE AND MONODISPERSITY	14
POLYSTYRENE CORE	14
HOLLOW SPHERE	15
PARAMETRIC STUDIES	16
POST-PROCESSING OF SILICA HOLLOW SPHERES.....	17
CHAPTER 4: CONCLUSION	18
SUMMARY OF RESULTS	18
FUTURE WORK RECOMMENDATIONS	18
REFERENCES	19
VITA.....	21

LIST OF TABLES

Table 3.1 Parametric studies	17
------------------------------------	----

LIST OF FIGURES

Figure 2.1 Silica Hollow Sphere Formation	8
Figure 2.2 Dispersion Polymerization Mechanism.....	9
Figure 2.3 Polymerization Process Stages	10
Figure 2.4 Hydrolysis and Condensation of TEOS Mechanism.....	11
Figure 2.5 TEM images of hollow silica spheres fabricated at different TEOS concentrations ..	11
Figure 2.6 Silica hollow spheres prepared at different ammonia concentrations	13
Figure 3.1 SEM images of PS particles A) Sample 3 diameter of 0.536 μm , B) Sample 4 average diameter of 0.952 μm	15
Figure 3.2 SEM images of silica hollow spheres A) Sample 3 average diameter of 0.545 μm , B)Sample 4 average diameter of 0.863 μm	15
Figure 3.3 Simultaneous silica coating formation and PS core dissolution process for hollow sphere formation	16
Figure 3.4 Post-processing procedure.....	17

CHAPTER 1: INTRODUCTION

RESEARCH MOTIVATION

This research was motivated by the need to develop functional materials that can improve efficiency of solar power generating devices. The use of renewable sources for power generation has gained interest in the last decades because of its multiple advantages. Renewable energy is always available and has multiple environmental benefits. Renewables require less maintenance compared to traditional fuel sources and can be produced locally contributing to U.S. energy independence. However, there is still significant limitations on the solar cell fabrication procedures and efficiency of the devices. Most materials and methods used for the fabrication of photovoltaic systems are toxic and harmful to the environment. Consequently, there is a need to improve the materials and processes for this purpose. Another big challenge of solar cells is the limited light transmittance from the sun to the solar cell. Research has been done to increase the solar light transmittance of photovoltaic systems using complex geometries.^{1,2} Although several new patterns have been explored, geometrical design of photovoltaic devices is extremely limited by traditional manufacturing. In addition, the conventional fabrication process is very complex and requires multiple materials for its preparation.³

Another challenge affecting solar cells performance is the large decrease on efficiency of photovoltaics when exposed to high relative humidity.⁴ Since photovoltaic systems are open to

¹ Sagil James and Rinkesh Contractor, "Study on Nature-Inspired Fractal Design-Based Flexible Counter Electrodes for Dye-Sensitized Solar Cells Fabricated Using Additive Manufacturing," *Scientific Reports* 8, no. 1 (2018), <https://doi.org/10.1038/s41598-018-35388-2>.

² Johnson Wong, "Griddler: Intelligent Computer Aided Design of Complex Solar Cell Metallization Patterns," 2013 IEEE 39th Photovoltaic Specialists Conference (PVSC), 2013, <https://doi.org/10.1109/pvsc.2013.6744296>.

³ Frederik C. Krebs, "Fabrication and Processing of Polymer Solar Cells: A Review of Printing and Coating Techniques," *Solar Energy Materials and Solar Cells* 93, no. 4 (2009): pp. 394-412, <https://doi.org/10.1016/j.solmat.2008.10.004>.

⁴ Tan, Cher Ming, Boon Khai Eric Chen, and Kok Peng Toh. "Humidity Study of a-Si PV Cell." *Microelectronics Reliability* 50, no. 9-11 (2010): 1871–74. <https://doi.org/10.1016/j.microrel.2010.07.021>.

atmosphere permanently, it is impractical to control or eliminate water exposure due to rain. Nonetheless, it is possible to decrease the impact of relative humidity on solar cells performance by incorporating a coating.

This research work aims the incorporation of silica hollow spheres (SHS) to photovoltaic systems through 3D printing technology as a hydrophilic coating to mitigate the lack of solar transmittance. The hydrophilicity of the SHS coating will increase the amount of sunlight passing through the solar cell by increasing the water dispersion in its surface. In addition, the hydrophilic coating exhibits an excellent self-cleaning effect helping to eliminate contamination of the surface. The implementation of additive manufacturing to the solar cell fabrication will also decrease the amount of materials and eliminate the toxicity of its production.

This thesis will present the synthesis and characterization of monodisperse SHS with controllable size via one-step process. The hydrophilic behavior of the SHS will act as a water dispersing material to help increase sunlight transmittance, in addition to decrease degradation of the cell by contamination. Furthermore, control size capabilities analyzed during this research expanded the use of SHS for other applications such energy absorption, thermal insulation and lightweight composites.

POWER GENERATION FROM RENEWABLE ENERGY SOURCES

Most of the current global energy is produced by coal and natural gas sources in power plants. However, this process represents a huge environment threat. Power plant emissions negatively impact air inducing problems such particle pollution, acid rain and ozone. Nevertheless, the global demand of electricity continues increasing, and therefore better and more efficient methods are needed to convert energy into electricity.

To resolve the negative environment impact by electricity generation, alternative methods to obtain energy from nature have been developed. Renewable energy is energy obtained from naturally repetitive and persistent flows of energy occurring in the local environment.⁵ According to the International Energy Agency (IEA), in 2018, 28% of the world net electricity was generated from renewable sources and is expected to increase up to 49% in the next 30 years.⁶ Renewables have gained interest because they require less and cheaper maintenance compared to traditional fuel sources. Electricity obtained from the environment can be produced locally, contributing to U.S. energy independence. In addition, renewable energy is clean and inexhaustible. The most popular types of renewable energy sources are biomass, hydropower, geothermal, wind and solar. In addition, the IEA expects wind and solar energy production to grow the fastest accounting over 70% of the total renewable energy generation.

SOLAR ENERGY

Over time, different technologies have been developed to convert electricity from solar energy.⁷ The most popular solar energy device is the solar or photovoltaic (PV) cell. PV cells are made from a semiconductor material used to absorb the photons emitted by the sun generating a flow of electrons or electrical current. This process does not produce energy pollution or carbon dioxide, but it has some limitations. The amount and quality of sunlight obtained worldwide is not

⁵ “U.S. Energy Information Administration - EIA - Independent Statistics and Analysis,” Renewable energy explained - U.S. Energy Information Administration (EIA), accessed June 1, 2020, <https://www.eia.gov/energyexplained/renewable-sources/>.

⁶ “U.S. Energy Information Administration - EIA - Independent Statistics and Analysis,” EIA projects that renewables will provide nearly half of world electricity by 2050 - Today in Energy - U.S. Energy Information Administration (EIA), accessed June 1, 2020, <https://www.eia.gov/todayinenergy/detail.php?id=41533>.

⁷ Furkan Dinçer, “The Analysis on Photovoltaic Electricity Generation Status, Potential and Policies of the Leading Countries in Solar Energy,” *Renewable and Sustainable Energy Reviews* 15, no. 1 (2011): pp. 713-720, <https://doi.org/10.1016/j.rser.2010.09.026>.

constant. The amount of sunlight is dependent on location, time, season and weather conditions. Therefore, there is a need to develop methods to increase the sunlight obtained by the solar cell.

MANUFACTURING OF SOLAR CELLS

Solar energy is “clean” energy, meaning that minimum to none contamination is produced during the power generation process. Conversely, the conventional fabrication process of solar energy-converting devices involves high-energy consumption, the use of several and toxic materials, and it generates material waste. A study developed by the Oak Ridge National Laboratory⁸, compares a conventional to an additive manufacturing process of a film device. The use of 3D printing technology eliminates most of the fabrication steps, production time, reduces waste and energy consumption. In addition, additive manufacturing is a non-contact deposition method, consequently, its applicable to an extensive range of materials such metals, ceramics, polymers and silicon. Additive manufacture provides multiple advantages to the overall photovoltaic fabrication process. Furthermore, the layer by layer assembly of 3D printing contributes to the easy use of different materials on each layer, facilitating also the addition of coatings.

EFFECT OF HUMIDITY ON SOLAR CELL PERFORMANCE

Besides the inconsistent operational conditions of solar cells, water exposure is one of biggest challenges of solar cells. A study developed by Hussein A Kazem⁹ in 2016 characterized

⁸ Pooran C. Joshi et al., “Direct Digital Additive Manufacturing Technologies: Path towards Hybrid Integration,” 2012 Future of Instrumentation International Workshop (FIIW) Proceedings, 2012, <https://doi.org/10.1109/fiiw.2012.6378353>.

⁹ Hussein A Kazem and Miqdam T Chaichan, “Effect of Humidity on Photovoltaic Performance Based on Experimental Study,” International Journal of Applied Engineering Research 10, no. 2015 (2016): pp. 43572-43577.

the negative impact of water contents on the solar irradiance and reduction of the solar intensity on photovoltaic cells. The study evaluated the impact of air temperature, relative humidity, wind speed and direction, and solar irradiance. The highest degradation of the photovoltaic cell was observed on relative humidity examinations compared to the other studied parameters. The study demonstrated the degradation of current, voltage, power and efficiency of the solar cell when exposed to high levels of humidity. Solar radiation is reduced at high levels of relative humidity. This is because water vapor forms a layer on the face of the solar cell blocking the sunlight transmittance, consequently, minimum to non-energy is converted.

SUPER-HYDROPHILIC COATING

In effort to improve the overall efficiency of solar cells under water exposure, researchers have developed different material designs of the active layer and employed inverted geometries.¹⁰ However, those procedures increase the amount of materials required for the solar cell fabrication and the overall complexity of the system.

This thesis aims the use of a hydrophilic coating to mitigate the negative impact of humidity on photovoltaic systems performance. A coating can be added to the solar cell surface without affecting the design or complexity of its fabrication. The inclusion of a hydrophilic coating will improve the overall efficiency of the system in multiple aspects. First, hydrophilicity disperses the water over the surface creating a thin uniform layer over the surface. Uniformity of the layer provides a clear unobstructed transmittance and overall better efficiency of the cell. Second, hydrophilic coatings also exhibit anti-fogging capabilities. The addition of the anti-fog characteristic reduces the lack of transmittance obtained by water vapor atmospheres. Lastly,

¹⁰ Pei Cheng and Xiaowei Zhan, "Stability of Organic Solar Cells: Challenges and Strategies," *Chemical Society Reviews* 45, no. 9 (2016): pp. 2544-2582, <https://doi.org/10.1039/c5cs00593k>.

previous studies have shown that hydrophilic coatings exhibit a self-cleaning effect.¹¹ In hydrophilic surfaces, water drops are dispersed to form a film of water. During the water spread, contaminant particles are washed away of the surface. The self-cleaning effect decreases the degradation of the solar cell and extends the lifespan of the photovoltaic system.

SILICA HOLLOW SPHERES

The fabrication of silica hollow spheres has gained interest because of their excellent properties for several applications. Silica hollow spheres are currently used in multiple chemical procedures such catalysis, chromatography, protection of active agents, fillers, waste removal and drug delivery.¹² In addition, the preparation of silica hollow spheres is an easy-replicable process and allows controllable diameter and wall thickness. Silica hollow spheres are usually produced using polymer particles as a template for a silica shell or coating, and final dissolution or calcination of the core. A detailed explanation of the synthesis process will be given on Chapter 2.

PROPERTIES OF SILICA HOLLOW SPHERES

Silica hollow spheres are characteristic for their ultralow density, high temperature resistance and super hydrophilicity. In addition, silica hollow spheres are have excellent chemical and thermal stability, high specific surface area, high porosity and lower thermal conductivity than air. Furthermore, hollow silica nanospheres have demonstrated exceptional antireflective and

¹¹ Swagata Banerjee, Dionysios D. Dionysiou, and Suresh C. Pillai, "Self-Cleaning Applications of TiO₂ by Photo-Induced Hydrophilicity and Photocatalysis," *Applied Catalysis B: Environmental* 176-177 (2015): pp. 396-428, <https://doi.org/10.1016/j.apcatb.2015.03.058>.

¹² M. Chen et al., "A Method for the Fabrication of Monodisperse Hollow Silica Spheres," *Advanced Materials* 18, no. 6 (2006): pp. 801-806, <https://doi.org/10.1002/adma.200501528>.

antifogging properties, they are non-toxic and highly resistant. The numerous properties of well-defined silica hollow spheres accredit them for multiple field applications.

APPLICATIONS OF SILICA HOLLOW SPHERES

Monodispersed silica particles have gained popularity on multiple physical chemistry applications such microwave absorption, electrocatalysis, hydrogen storage and lithium ion batteries. Silica hollow spheres are also present in different industries such pharmacy as drug deliver medium, pigments and photographic emulsions. As a result of the ultralow density of the silica particles, they are excellent for lightweight purposes of heavy materials such ceramics and metals. Additionally, silica nanoparticles are excellent antireflective and antifogging coatings currently used on windows, optical devices and photovoltaics.

CHAPTER 2: FABRICATION OF SILICA HOLLOW SPHERES

INTRODUCTION

Although multiple methods have been developed for the synthesis of silica hollow spheres, Kolbe's method remains the most popular and effective. Kolbe¹³ first formed silica hollow spheres through the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in an aqueous ammoniacal alcohol medium. Although multiple improvements in Kolbe's process have been reported, most of them concur in the following technique. A typical synthesis of silica hollow spheres consists of: an initial preparation of monodisperse polystyrene particles, usually achieved by dispersion polymerization; a subsequent formation of a silica shell onto the PS particles, obtained by hydrolysis and condensation of TEOS; and a final dissolution or calcination of the PS core.

During this research work, Chen's method was selected for the preparation of silica hollow spheres for multiple reasons. First, the synthesis of the hollow spheres takes place in a single step. Meaning, the particle preparation and hydrolyzation of TEOS occur in the same medium (no exchange of the solvent is required). Second, no calcination is required because the PS particle is dissolved in the medium. Lastly, the elimination of the second medium and calcination process reduces the production time, amount of chemicals required, and overall fabrication cost.

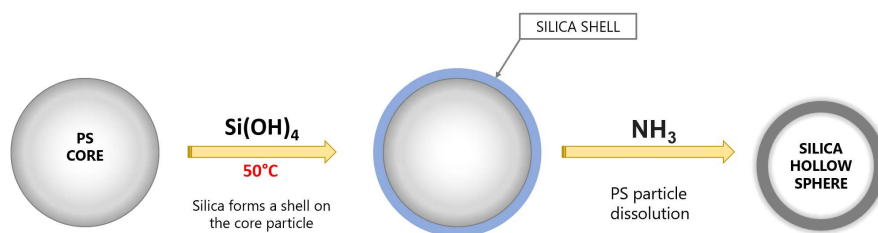


Figure 2.1 Silica Hollow Sphere Formation

¹³ Kolbe, G. "The Complex Chemical Behavior of Silica." Dissertation, 1956.

POLYSTYRENE PARTICLE PREPARATION

Monodisperse polystyrene particles can be fabricated by dispersion polymerization of styrene. Dispersion polymerization is a type of precipitation polymerization commonly used to combine multiple monomers to form a polymer. During this process, a free radical or initiator is added to a monomer double bond forming a new radical. The new radical is added to a new monomer double bond to form a chain of monomers, or oligomer. This mechanism continually repeats until a large molecule, or polymer is completely formed.

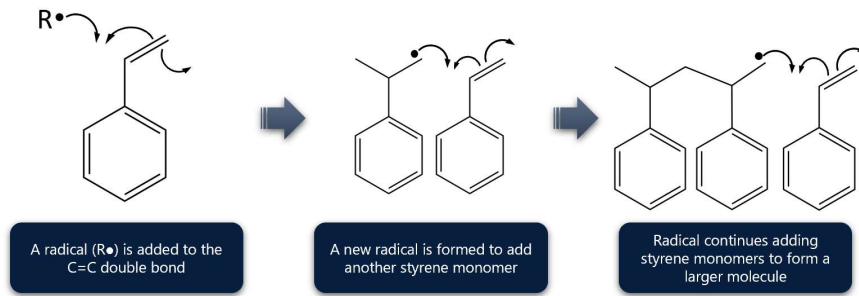


Figure 2.2 Dispersion Polymerization Mechanism

DISPERSION POLYMERIZATION

Dispersion polymerization for this thesis work was developed in five main stages. During the first stage, a monomer, residual stabilizer, and initiator are mixed together to form a homogeneous phase in an alcohol medium. The second stage is the oligomer formation or polymerization initiation. The third stage is responsible for the particle nuclei formation, subsequently stabilized in stage four. During the last stage, the particle growth is observed until the polymerization is completed.

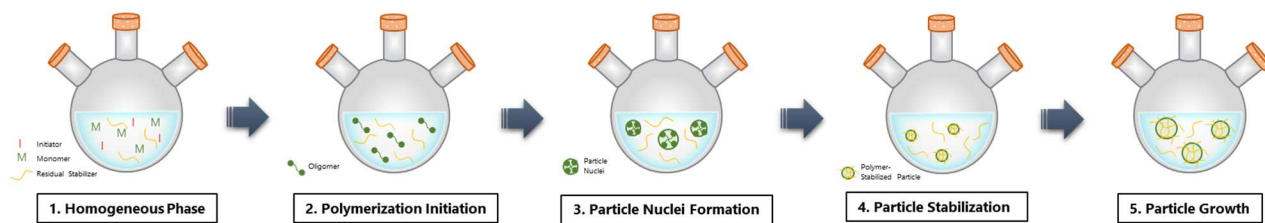


Figure 2.3 Polymerization Process Stages

EXPERIMENTAL PROCEDURE

The preparation of monodisperse PS particles was done by dispersion polymerization in a three-necked flask connected to a condenser, a thermocouple, and a heating mantle. Initially, 1.5 g of stabilizer (PVP), 0.2 g of AIBN, 5 g of DI water, and 5 g of styrene were mixed with 22.5 g of solvent, specified on each trial, in the three-neck flask. Next, the reaction was deoxygenated by continually running Nitrogen gas through the system. After the deoxygenation process was done for 30 minutes, the reaction was mixed with a stirring bar at 100 rpm and heated to 70°C. Succeeding 1.5 hours, 5 g of styrene and the 22.5 g of solvent were added to the homogeneous mixture. The polymerization was conducted for 24 hours and a sample was obtained with a pipet from the medium for characterization. Then, the reaction was cooled to 50°C and nitrogen gas was closed. Lastly, the subsequently specified concentrations of ammonia and TEOS were added to the three-neck flask and the mixture was continuously stirred for 1 hour.

HYDROLYSIS AND CONDENSATION OF TEOS

Tetraethyl orthosilicate (TEOS) is fundamental for the production of the silica coating. The silica coating or shell formation is contributed to three primary steps as shown in Figure 2.4. First, TEOS is hydrolyzed in an ammoniacal alcohol medium. Ammonia is used as a catalyst in the reaction producing a mixture of ethanol and ethoxysilanol. Second, continuous hydrolysis and

subsequent condensation of the ethoxy groups lead to crosslinking. Lastly, silica particles are achieved by the loss of water.

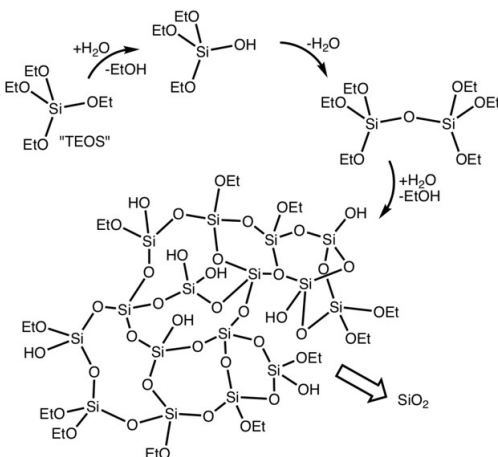


Figure 2.4 Hydrolysis and Condensation of TEOS Mechanism

EFFECT OF TEOS CONCENTRATION ON SILICA HOLLOW SPHERES

Besides the primary function of TEOS as a silica developer, the ethyl ester is also responsible for the hollow sphere thickness and appearance. Although the wall thickness can be easily tailored by modifying the TEOS concentration during the hollow sphere fabrication, excess of TEOS can cause serious deformations of the surface, as well as secondary nucleus formation. In Figure 2.5, the SEM images of three different concentrations (6, 9, and 12 g) are shown based on Chen's research work.

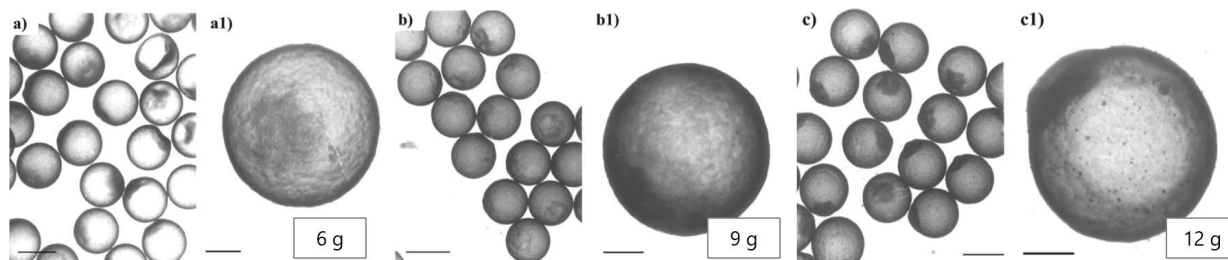


Figure 2.5 TEM images of hollow silica spheres fabricated at different TEOS concentrations

The first SEM image shows a hollow silica sphere with ~ 50 nm wall thickness fabricated with 6 g of TEOS. When the concentration of TEOS was increased to 9 g (second image), the wall thickness of the sphere doubled the previously obtained size. However, when 12 g of TEOS was added, deformation of the silica shell and secondary nucleation were observed. Based on the experimental results, it is possible to control the sphere wall thickness by modifying the TEOS concentration.

POLYSTYRENE PARTICLE DISSOLUTION

The last step of the silica hollow sphere fabrication is the elimination of the PS core. During this stage, the PS core is dissolved and gradually diffused out of the silica shell. The diffusion of the polymer is possible due to the synchronized formation of the shell and dissolution of the core when reacted with ammonia.

EFFECT OF AMMONIA CONCENTRATION ON SILICA HOLLOW SPHERES

The concentration of ammonium hydroxide is critical for the synthesis of silica hollow spheres due to two main reasons. First, the ammonia is responsible for the dissolution of the PS core during the formation of the silica shell. Second, the ammonia acts as a catalyst during the hydrolysis and condensation of TEOS. Although the hydride is crucial for the successful achievement of both, the hydrolysis and condensation of TEOS and the dissolution of the PS core, the ammonia concentration needs to be controlled to avoid premature or non-elimination of the PS particle.

In Figure 2.6, the effect of three different ammonia concentrations on the preparation of silica hollow spheres is shown. Picture a demonstrates how the PS core was not completely dissolved

when mixed with less than 2 ml of ammonia. Picture b shows the complete dissolution of the core when 3 ml were added to the reaction. On picture c, seriously deformed and collapsed spheres were obtained when exposed to more than 4 ml.

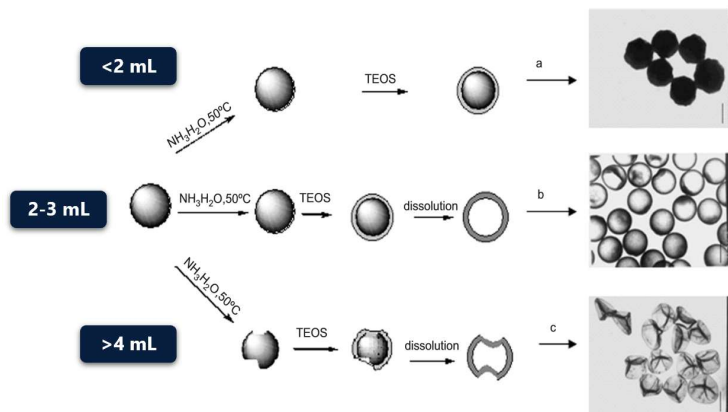


Figure 2.6 Silica hollow spheres prepared at different ammonia concentrations

CHAPTER 3: RESULTS

INTRODUCTION

This chapter will describe the synthesis methodology used for the fabrication of silica hollow spheres, as well as the parametric studies and post-processing of the trials. During this research work, two main aspects of the preparation of the hollow spheres were evaluated: size increase and monodispersity. The ability to control hollow spheres' size and dispersity of the particles expands their range of applications and accentuates the properties of the material. Six trials were conducted during this experiment, analyzing the PS core and hollow sphere outcomes independently. The technique utilized is discussed in the following sections.

SIZE INCREASE AND MONODISPERSITY

During this research work, a method to increase hollow spheres size and monodispersity was developed. Two different solvents were used for the preparation of silica hollow spheres in order to increase the PS particle size. The impact of the different mediums on the PS core and Hollow sphere fabrication is discussed independently next.

POLYSTYRENE CORE

Initially, ethanol was used as the only solvent in the medium for the synthesis, and PS particles of 0.536 μm were successfully obtained. However, when a combination of 50% ethanol and 50% 2-methoxyethanol were utilized, PS particles of 0.952 μm were achieved. The size increase is due to the increase in the overall molecular weight of the medium. The molecular weight of 2-methoxyethanol is 76.09 g/mol, compared to 46.07 g/mol of ethanol. The use of high molecular weight solvents decreases the reaction rate of the chemical process extending the

particle nuclei formation stage of the polymerization process. The elongation of this stage resulted in monodisperse larger particles due to the slower formation rate.

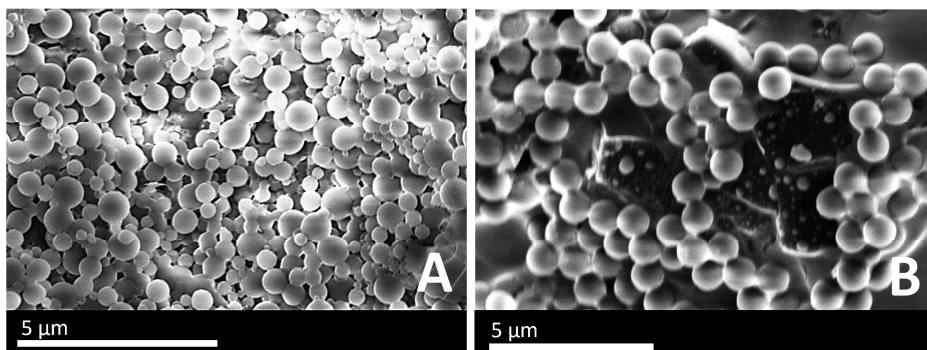


Figure 3.1 SEM images of PS particles A) Sample 3 diameter of 0.536 μm , B) Sample 4 average diameter of 0.952 μm .

HOLLOW SPHERE

The PS particles obtained from samples 3 and 4 were used as a core for the preparation of silica hollow spheres. As expected, sample 4 silica hollow spheres were considerably larger than the spheres obtained by sample 3. However, only a 58% size increase was observed when comparing both samples' hollow spheres. Hollow spheres with averages diameters of 0.545 μm and 0.863 μm were obtained from samples 3 and 4, respectively. Also, an improvement in dispersity of the spheres was observed in sample 4 as shown in Figure 3.1.

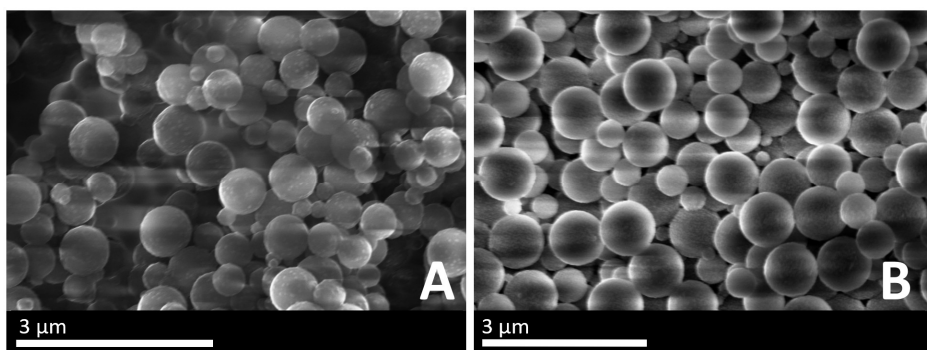


Figure 3.2 SEM images of silica hollow spheres A) Sample 3 average diameter of 0.545 μm , B) Sample 4 average diameter of 0.863 μm .

A negative size difference between the PS particles and the hollow spheres is observed in sample 4. The size reduction is a consequence of the silica shell's ambition to be formed on the core surface. Since the formation of the core and the dissolution of the shell are simultaneous processes, the shell is attracted to the PS core surface until the Silica coating is fully formed, then, the PS core is completely dissolved. Under those circumstances, a small “shrinkage” is observed as an aftereffect as shown in Figure 3.2.

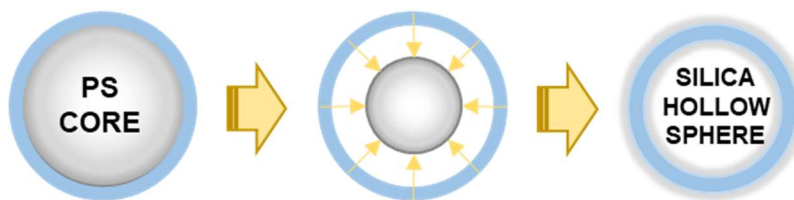


Figure 3.3 Simultaneous silica coating formation and PS core dissolution process for hollow sphere formation

PARAMETRIC STUDIES

This experiment consisted of the fabrication of six different samples. The results obtained from the first sample (T1) did not show the presence of any particles or spheres. Consequently, the ammonia concentration was decreased to 1.5 g to control the dissolution rate of the PS particle. After decreasing the ammonia amount, silica hollow spheres of approximately x.x average diameter were obtained in sample T2. For the fabrication of sample T3, the styrene amount was decreased by 50% in order to change the Styrene-PVP ratio. The change was done with the main purpose of extending the polymerization initiation stage for a longer period. In addition, the ammonia concentration was increased to 2.5 g to ensure the entire dissolution of the core. A 0.545 μm average diameter silica hollow spheres were obtained in sample T3. To further increase the particle size, the molecular weight of the reaction medium was increased by using a 50% ethanol 50% 2-methoxyethanol solvent mixture as shown in sample T4. Silica hollow spheres of 0.863 μm

average diameter were successfully fabricated in sample T4. In sample T5, a combination of 50% 2-methoxyethanol and 50% methanol were utilized to further increase the medium overall molecular weight. Lastly, methanol was used as the only solvent for the preparation of sample T6. A full description of the parametric studies is described in Table 3.1.

Table 3.1 Parametric studies

Sample	DI Water	Ethanol	2-Methoxy ethanol	Styrene	Methanol	PVP	Ammonia	MTC	AIBN	TEOS
T1	5 g	45 g	-	10 g	-	1.5 g	3 g	0.39 g	0.2 g	9 g
T2	5 g	45 g	-	10 g	-	1.5 g	1.5 g	0.39 g	0.2 g	9 g
T3	5 g	45 g	-	5 g	-	1.5 g	2.5 g	0.39 g	0.2 g	9 g
T4	5 g	22.5 g	22.5 g	5 g	-	1.5 g	2.5 g	0.39 g	0.2 g	9 g
T5	5 g	-	22.5 g	5 g	22.5 g	1.5 g	2.5 g	0.39 g	0.2 g	9 g
T6	5 g	-	45 g	5 g	-	1.5 g	2.5 g	0.39 g	0.2 g	9 g

POST-PROCESSING OF SILICA HOLLOW SPHERES

After the fabrication process of the silica hollow spheres was completed, the obtained heterogeneous mixture was cooled down to room temperature. Afterward, the mixture was centrifuged at 3000 rpm for 30 minutes. Subsequently, the spheres were washed with ethanol and vortex-mixed for 5 minutes and repeatedly centrifuged. The washing process was repeated two times to ensure the reliability of the characterization of the samples.



Figure 3.4 Post-processing procedure

CHAPTER 4: CONCLUSION

SUMMARY OF RESULTS

This thesis was focused on the fabrication of monodisperse silica hollow spheres through a single-step process. The synthesis consisted of three main stages: the polymerization process and PS particle preparation, the silica coating onto the PS particle, and the dissolution of the PS core. During the production of the hollow spheres, different solvents were used to increase the molecular weight of the medium resulting in a slower reaction rate. The reaction rate was slowed with the main objective of extending the particle nuclei formation stage of the polymerization. The effect of the medium molecular weight increase on the PS particle size and dispersity of the spheres was evaluated during this research. A size increase of 77.6% on the PS particle and 58% on the silica hollow spheres were achieved demonstrating a successful slowed reaction rate. In addition, the dispersity of both, the PS particle and the hollow spheres was significantly improved by increasing the molecular weight of the medium.

FUTURE WORK RECOMMENDATIONS

Although this research work demonstrated a successful method for size increase on the particle size, further analysis to achieve tunable sizes is needed. Optimizing parameters can be utilized to develop guidelines for tailored particle sizes. In addition, the fabricated silica hollow spheres' thermal and mechanical properties can be evaluated for potential industrial applications. Moreover, utilize the synthesized hollow spheres to fabricate composites using additive manufacturing techniques. Lastly, the thermal insulation and energy absorption properties of the silica hollow spheres can be evaluated for additional applications.

REFERENCES

- James, Sagil, and Rinkesh Contractor. "Study on Nature-Inspired Fractal Design-Based Flexible Counter Electrodes for Dye-Sensitized Solar Cells Fabricated Using Additive Manufacturing." *Scientific Reports* 8, no. 1 (2018). <https://doi.org/10.1038/s41598-018-35388-2>.
- Wong, Johnson. "Griddler: Intelligent Computer Aided Design of Complex Solar Cell Metallization Patterns." 2013 IEEE 39th Photovoltaic Specialists Conference (PVSC), 2013. <https://doi.org/10.1109/pvsc.2013.6744296>.
- Krebs, Frederik C. "Fabrication and Processing of Polymer Solar Cells: A Review of Printing and Coating Techniques." *Solar Energy Materials and Solar Cells* 93, no. 4 (2009): 394–412. <https://doi.org/10.1016/j.solmat.2008.10.004>.
- Tan, Cher Ming, Boon Khai Eric Chen, and Kok Peng Toh. "Humidity Study of a-Si PV Cell." *Microelectronics Reliability* 50, no. 9-11 (2010): 1871–74. <https://doi.org/10.1016/j.microrel.2010.07.021>.
- "U.S. Energy Information Administration - EIA - Independent Statistics and Analysis." *Renewable energy explained - U.S. Energy Information Administration (EIA)*. Accessed June 1, 2020. <https://www.eia.gov/energyexplained/renewable-sources/>.
- "U.S. Energy Information Administration - EIA - Independent Statistics and Analysis." *EIA projects that renewables will provide nearly half of world electricity by 2050 - Today in Energy - U.S. Energy Information Administration (EIA)*. Accessed June 1, 2020. <https://www.eia.gov/todayinenergy/detail.php?id=41533>.

- Dinçer, Furkan. “The Analysis on Photovoltaic Electricity Generation Status, Potential and Policies of the Leading Countries in Solar Energy.” *Renewable and Sustainable Energy Reviews* 15, no. 1 (2011): 713–20. <https://doi.org/10.1016/j.rser.2010.09.026>.
- Joshi, Pooran C., Ryan R. Dehoff, Chad E. Duty, William H. Peter, Ronald D. Ott, Lonnie J. Love, and Craig A. Blue. “Direct Digital Additive Manufacturing Technologies: Path towards Hybrid Integration.” 2012 Future of Instrumentation International Workshop (FIIW) Proceedings, 2012. <https://doi.org/10.1109/fiiw.2012.6378353>.
- Kazem, Hussein A, and Miqdam T Chaichan. “Effect of Humidity on Photovoltaic Performance Based on Experimental Study.” *International Journal of Applied Engineering Research*, 23, 10, no. 2015 (2016): 43572–77. <https://doi.org/http://www.ripublication.com>.
- Cheng, Pei, and Xiaowei Zhan. “Stability of Organic Solar Cells: Challenges and Strategies.” *Chemical Society Reviews* 45, no. 9 (2016): 2544–82. <https://doi.org/10.1039/c5cs00593k>.
- Banerjee, Swagata, Dionysios D. Dionysiou, and Suresh C. Pillai. “Self-Cleaning Applications of TiO₂ by Photo-Induced Hydrophilicity and Photocatalysis.” *Applied Catalysis B: Environmental* 176-177 (2015): 396–428. <https://doi.org/10.1016/j.apcatb.2015.03.058>.
- Chen, M., L. Wu, S. Zhou, and B. You. “A Method for the Fabrication of Monodisperse Hollow Silica Spheres.” *Advanced Materials* 18, no. 6 (2006): 801–6. <https://doi.org/10.1002/adma.200501528>.
- Kolbe, G. “The Complex Chemical Behavior of Silica.” Dissertation, 1956.

VITA

Hilda Fontes was born in El Paso, Texas, in 1993. She grew up in Ciudad Juárez, Chihuahua, México, and completed her high school studies at the Preparatoria “El Chamizal”. In 2014, Hilda started her undergraduate degree in Chemical Engineering at the New Mexico State University. Four years after, she obtained her bachelor’s degree as well as a minor in Chemistry in May 2018. In fall 2018, she continued her academic studies joining the Master’s program in Mechanical Engineering at the University of Texas at El Paso. Hilda worked as a teacher and research assistant during her graduate education focusing her research on fabrication of piezoelectric ceramics and chemical synthesis of hollow spheres. In June 2019, she obtained the NNSA Graduate Fellowship and served as a general engineer at Nevada Field Office in Las Vegas, Nevada while continuing her graduate studies.

Contact Information: hilda.fontes@gmail.com