SURFACE ENGINEERING OF NANOPARTICLES BY PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

A Dissertation in
Chemical Engineering
by
Anaram Shahravan

© 2012 Anaram Shahravan

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2012
The dissertation of Anaram Shahravan was reviewed and approved* by the following:

Themis Matsoukas  
Professor of Chemical Engineering  
Dissertation Advisor, Chair of Committee

Joan Redwing  
Professor of Materials Science and Engineering

Darrell Velegol  
Professor of Chemical Engineering

Robert Rioux  
Friedrich G. Helfferich Assistant Professor

Andrew Zydney  
Walter L. Robb Chair and Professor of Chemical Engineering  
Head of the Department of Chemical Engineering

*Signatures are on file in the Graduate School.
Abstract

Altering near-surface properties of nanoparticles or nanopowders without affecting their desirable bulk characteristics has attracted attention in many industries. Among different approaches that have been used to modify surface properties, plasma enhanced chemical vapor deposition is discussed in this dissertation. This work focuses on adapting plasma polymer coating on the surface of micro- and nano-sized particles in a dry environment. Plasma deposited polymer on the surface of nanoparticles improves their physical and chemical properties, and also provides a barrier for encapsulation, protection, and also a source to attach new organic functional groups to change the chemistry of the surface. Another important achievement of this work is introducing a very novel condition to produce responsive particles in the plasma. Deposition process in plasma can be controlled by different parameters such as reactor pressure, hydrocarbon flow rate, and plasma generator power. Here, conditions to produce thin-films or synthesis of responsive nanoparticles are discussed.

Core-shell nanostructures were synthesized by plasma deposition in a radio-frequency plasma reactor. Silica and KCl nanoparticles are encapsulated by depo-
sition of isopropanol-based films of amorphous hydrogenated carbon. By control-
ling the deposition time, under constant deposition rate of 1 nm/min, particles are 
encapsulated in a layer of plasma polymer with thickness between 15 and 100 nm. 
Films are robust, chemically inert, and thermally stable up to 250°C. The perme-
ability of the shells is determined by depositing films of various thickness onto KCl 
nanoparticles and monitoring the dissolution of the core in aqueous solution. The 
dissolution profile is characterized by an initial rapid release, followed by a slow 
release that lasts up to 30 days for the thickest films. The profile is analyzed by 
Fickian diffusion through a spherical matrix. We find that this model captures very 
accurately the entire release profile except for the first 12 hours during which, the 
dissolution rate is higher than that predicted by the model. The overall diffusion 
coefficient for the dissolution of KCl is $3 \times 10^{-21} \text{m}^2/\text{s}$.

Wetting characteristics of nanoparticles are also tuned using plasma enhanced 
chemical vapor deposition technique. The plasma polymer coating impart the 
properties of the precursors used in the plasma technique, without the requirement 
for nanoparticle surface preparation. For a range of chosen precursors, the water 
contact angle of a sessile droplet on coated copper oxide nanoparticles is shown to 
vary from 54° to 76°, 92°, and 108°. Stable suspensions of coated nanoparticles are 
fabricated and are studied to be used as nanofluids. These fluids that contain fine 
nanoparticles are widely used as heat transfer liquid because of their thermal con-
ductivity enhancement due to the existence of the particles. Thermal conductivity 
of stable suspensions of silica and copper oxide is studied for different nanofluids 
with polar and non-polar solvents, oils and refrigerants, as their base fluid. 

Hydrophobic coatings are tailored as a passivating thin-film for aluminum
nanoparticles as well. Since they repel water, no thick oxide layer can form on their surfaces. Coated particles are kept in a harsh environment with high humidity and their aluminum content is measured using thermogravimetric analysis. Experimental data reveals that particles are protected against contamination and oxidation. Aluminum particles are the prime candidate as an additive to propellent, combustibles, and explosives due to their high enthalpy of combustion. Deposition of plasma polymer coating also improves their combustion by releasing high energy at elevated temperatures.

Hydrocarbon plasmas are known to produce particles and films consisting of cross-linked amorphous hydrogenated carbon. Here, we document the formation of liquid-like particles which subsequently solidify via a process that releases hydrogen and produces a solid microbubble with micron-size diameter, nanometer-size shell thickness, and high volume fraction, in excess of 90%. These materials are produced in a toluene plasma under conditions that promote low degree of cross-linking (low power, high pressure). Liquid-like droplets produced under these conditions are seen to blow up in TEM under irradiation by the electron beam and to produce solid bubbles with diameter of about 3 µm. The solid-to-liquid transformation is also observed under laser irradiation of sufficient power, as well as under heating. We present evidence that the formation of these microbubbles is due to solidification of the liquid-like precursor that is accompanied by release of hydrogen. This mechanism is confirmed by a simple model that provides quantitative description of the particle size before and after solidification. These unique stimuli-responsive particles exhibit the potential of using temperature, electron beam, or laser as a tool to change their size and structure which may find application in thermal
insulators, lightweight materials and light scattering agents.
# Table of Contents

List of Figures xi

List of Tables xv

Acknowledgments xvi

Chapter 1 Introduction 1
   1.1 Nanoparticles 2
   1.2 Plasma Enhanced Chemical Vapor Deposition 6
       1.2.1 Plasma Polymerization 8
   1.3 Characteristics of Plasma Polymer Films 11
       1.3.1 Permeability and Encapsulation Properties of Amorphous
            Hydrogenated Carbon Films 12
       1.3.2 Hydrophobicity of Amorphous Hydrogenated Carbon and
            Fluorocarbon Thin-Films 13
       1.3.3 Passivating Properties of Amorphous Hydrogenated Carbon
            Films 14
   1.4 Nanoparticle Fabrication in Plasma 15
   1.5 Research Goals 16
   1.6 Dissertation Outline 17

Chapter 2 Experimental Procedure 21
   2.1 Construction of the Experimental Setup 21
       2.1.1 Different Configurations of the Reactors 21
       2.1.2 Vacuum System 23
       2.1.3 Flow Controllers 23
       2.1.4 Plasma Power System 25
### Chapter 2

2.2 Protocol of the System Operation .......................... 25  
2.2.1 Preparation of the Vacuum System ..................... 25  
2.2.2 Operating the Plasma Deposition Process .......... 26  
2.3 Reactor Cleaning ........................................... 26  
2.4 Materials Characterization Techniques ................. 27  
2.4.1 Transmission Electron Microscopy .................... 27  
2.4.2 Scanning Electron Microscopy ......................... 28  
2.4.3 Dynamic Light Scattering ............................. 28  
2.4.4 Zeta Potential Measurements ......................... 29  
2.4.5 Thermogravimetric Analysis and Differential Scanning Calorimetry ......................... 29  
2.4.6 Fourier Transform Infrared Spectroscopy (FTIR) .... 29  
2.4.7 Water Contact Angle Measurements ................. 30  
2.4.8 Thermal Conductivity Measurements ................. 30

### Chapter 3

Encapsulation and Controlled Release from Core-Shell Nanoparticles Fabricated by Plasma Polymerization 32

3.1 Introduction .................................................. 32  
3.2 Experimental ................................................ 35  
3.2.1 Materials ................................................. 35  
3.2.2 Silica and Potassium Chloride Particle Preparation .. 35  
3.2.3 Deposition Technique: PECVD for Synthesis of Core-shell Structure ......................... 36  
3.2.4 Dissolution of Core Materials ......................... 38  
3.3 Results and Discussion .................................... 39  
3.3.1 Hollow Particle Size and Morphology ................ 39  
3.3.2 Release Profile of Coated KCl Particles ............... 42  
3.3.3 Analysis of Release Profiles .......................... 47  
3.4 Conclusions ............................................... 50

### Chapter 4

Controlled Manipulation of Wetting Characteristics of Nanoparticles with Dry-based Plasma Polymerization Method 52

4.1 Introduction ................................................. 52  
4.2 Experiments ................................................. 54  
4.3 Results and Discussion .................................... 56  
4.4 Conclusions ............................................... 63
Chapter 5  Development of Hydrophobic Coatings for Oil- and Refrigerant-based Nanofluid by Plasma Deposition  64
  5.1  Introduction ..................................................  64
  5.2  Experimental ..................................................  67
      5.2.1  Preparation of Dry Nanoparticles .......................  67
      5.2.2  Particle Coating .........................................  67
      5.2.3  Preparation of Nanofluids .............................  69
  5.3  Results and Discussions .....................................  69
  5.4  Conclusions ..................................................  80

Chapter 6  Passivation of Aluminum Nanoparticles  82
  6.1  Introduction ..................................................  82
  6.2  Experiment ....................................................  86
      6.2.1  Materials and Preparations .............................  86
      6.2.2  Plasma Coating of Aluminum Nanoparticles .............  86
      6.2.3  Characterization of Coated Nanoparticles ...............  88
  6.3  Results and Discussions .....................................  88
  6.4  Conclusions .................................................. 102

Chapter 7  Microbubble Formation from Plasma Polymers  103
  7.1  Introduction .................................................. 103
  7.2  Experimental .................................................. 105
      7.2.1  Synthesis ................................................ 105
      7.2.2  Characterizations ....................................... 107
  7.3  Results ....................................................... 108
  7.4  Discussion ................................................... 115
  7.5  Conclusions .................................................. 120

Chapter 8  Conclusions and Recommendations for Future Work  122
  8.1  Conclusions .................................................. 122
  8.2  Recommendations for Future Work ........................... 126
      8.2.1  Experimental Set-up ................................... 126
      8.2.2  Encapsulation Strategies ............................... 127
      8.2.3  Protective Thin-film on Wafers ......................... 128
      8.2.4  Formation of Particles in Plasma and Their Application in Nanofluids ......................... 129
      8.2.5  Formation of Microbubbles ............................. 130
Appendix A Particle Preparation
  A.1 Silica Particles .................................................. 131
    A.1.1 Dry Silica ................................................... 131
    A.1.2 Colloidal Silica ........................................... 132
  A.2 Sodium Chloride and Potassium Chloride ...................... 132
  A.3 Aluminum ........................................................ 133
  A.4 Copper Oxide .................................................... 133

Appendix B Fick’s Law for Spherical Coordinate .................... 135

Appendix C Derivation of Relationship Between Bubble Initial
  and Final Radius .................................................... 138

Bibliography .............................................................. 141
List of Figures

1.1 Molecular structure of polyethylene (conventional polymer), and hypothetical structure of a hydrocarbon plasma polymer [1]. 9
1.2 Schematic of entire step-growth mechanism of plasma polymerization [2]. 10
1.3 Phase diagram of film and powder formation in ethylene discharge at 100 W [3]. 16

2.1 Description of the (a) horizontal tubular reactor and (b) vertical reactor. 22
2.2 A schematic of the plasma enhanced chemical vapor deposition set-up used for the present work. 24

3.1 Schematic diagram of the experimental set-up used for nanoparticle coating. 37
3.2 TEM images of coated silica particles with diameter of (a),(b) 200 nm, and (c) 1000 nm. Coating thickness is 9.3±2.3 nm, 15±4.7 nm, and 12±4.5 nm respectively. Scale bar= 100 nm. 39
3.3 Shell thickness on the surface of KCl particles exposed to the same plasma for different coating time. 40
3.4 TEM images of hollow particles after etching the silica core with diameter of 200 nm. 41
3.5 Field emission scanning electron micrograph of hollow particles after etching the silica core and 10 minutes of sonication. 43
3.6 Field emission scanning electron micrograph of half shells after etching the silica core. 44
3.7 Thermogravimetric analysis (TGA) profile of the hollow particles. Transmission electron micrographs of hollow particles at (a) 100°C, (b) 250°C, and (c) 350°C. Scale bar= 100 nm. 45
3.8 Transmission electron micrographs of coated KCl particles which are dissolved in water for: (a) 0 minute, (b) 5 minutes, (c) 1 hour, (d) 6 hours, (e) 1 day, and (f) 6 days. Scale bar= 100 nm. 46
3.9 Effect of shell thickness on the release profile. The inset graph shows the release during the first hour. ........................................... 47
3.10 Linearized plot of fractional release according to Eq. (3.2). ....... 48
3.11 Comparison of experimental and fitted profiles. Lines are fits to Eqn. 3.2. The inset graph shows the calculated diffusion coefficients. ............................................................ 49

4.1 Schematic of the procedure for nanoparticle preparation, PECVD coating, and dispersion of nanoparticles in different solvents. ....... 55
4.2 Transmission electron micrographs of (a) silica particles coated with IPA, (b) silica particles coated with toluene, (c) silica particles coated with PFD plasma polymer. ........................................... 57
4.3 Transmission electron micrographs of (a) uncoated copper oxide particles, (b) copper oxide particles coated with IPA, (c) copper oxide particles coated with toluene, and (d) copper oxide particles coated with PFD plasma polymer. ........................................... 58
4.4 Left column shows the contact angle measurements on the surface of coated wafers with different plasma polymers and right column shows spin-coated wafers with coated copper oxide particles. Sessile water droplet contact angle measurements on the (a) uncoated, (b) IPA coated (c) toluene coated, (d) PFD coated, (e) copper oxide spine-coated, (f) IPA copper oxide spin-coated, (g) toluene copper oxide spin-coated, (h) PFD copper oxide spin-coated silicon wafer. (i) shows contact angle for different coatings on the surface of a silicon wafer or coated nanoparticles. ........................................... 60
4.5 FTIR spectra for toluene, isopropyl alcohol, and perfluorodecalin plasma polymerized coating. ........................................... 61

5.1 Field emission scanning electron micrographs of (a) silica nanoparticles and (b) copper oxide nanoparticles. ........................................... 70
5.2 Copper oxide particle size distribution. ........................................... 71
5.3 Transmission electron micrographs of coated copper oxide (CuO) with toluene and perfluorodecalin. ........................................... 72
5.4 Miscibility of coated copper oxide particles with water. (a) uncoated copper oxide, (b) coated copper oxide with IPA, (c) coated copper oxide with toluene, (d) coated copper oxide with perfluoron-octane, (e) coated copper oxide with perfluorodecalin mixed with water. ........................................... 73
5.5 Size of (a) silica and (b) copper oxide nanoparticles measured in different solvents coated with different materials. ................. 74
5.6 Coated silica with perfluorodecalin dispersed in dodecane. (a) Size of the particles for different sonication time and (b) size of the particles after 50 minutes of sonication. .................................................. 76

5.7 The experimental result represented by dot symbol for conductivity of (a) coated silica particles with IPA in ethylene glycol (b) coated copper oxide particles with IPA in ethylene glycol, and (c) coated copper oxide particles with toluene in dodecane. The solid and dashed line denote the Maxwell classical bounds for thermal conductivity of nanofluids. ............................................. 78

5.8 Time characteristics of coated CuO in PAO. ............................. 79

6.1 Schematic of the plasma deposition process illustrating precursor delivery system, vacuum and pressure controllers, glass reactor, and RF generator. .......................................................... 88

6.2 Transmission electrom micrographs of aluminum particles coated with (a) isopropyl alcohol (b) toluene, (c) perfluorodecalin plasma polymer ................................................................. 90

6.3 Water contact angle measurements of coated silicon wafer with isopropyl alcohol (IPA), toluene, and perfluorodecalin (PFD). ......... 91

6.4 Profile release of coated KCl with toluene, and IPA in water. IPA coating is not hydrophobic and is permeable to water, so the solid line shows its controlled release over time. Toluene coating is hydrophobic, therefore the profile release just show small amount of KCl that was dissolve just after mixing KCl particles with water. None of the core material was dissolve as shown by dashed line. .......... 92

6.5 SEM images of (a) uncoated aluminum wafer, (b) uncoated aluminum wafer exposed to NaOH, (c) and coated aluminum which is exposed to NaOH. ..................................................... 93

6.6 Field emission scanning electron micrographs of aluminum particles that were (a) transferred from glove box to a sealed container, (b) exposed to air and humidity, and (c) coated with perfluorodecalin and were exposed to humidity and air. ........................................ 95

6.7 Transmission electron micrographs of aluminum particles that were (a) transferred from glove box to a sealed container, (b) exposed to air and humidity, and (c) coated with perfluorodecalin and were exposed to humidity and air. ................................. 96

6.8 Energy dispersive spectroscopy (EDS) graphs of Al nanoparticles (a) uncoated kept in glovebox, (b) uncoated exposed to air and humidity, and (c) coated with PFD plasma polymer exposed to air and humidity. ........................................ 97
6.9 TGA graph of uncoated Al and coated Al placed in the same environment after a month with RH of 90%. 99
6.10 DSC graphs of uncoated Al stored in a glovebox and coated Al with different coatings placed in the air after a month with RH of 90%. 100
7.1 Schematic representation of the vertical glass reactor used for plasma process to produce nanoparticles with the picture of the reactor. 107
7.2 Transmission electron micrographs of (a) a single 480 nm plasma polymerized toluene particle before exposing to electron beam, and (b) same particles after exposing to electron beam. 109
7.3 Transmission electron micrographs of a single 3.23 µm toluene plasma polymer at (a) 0.6, (b) 1.05, (c) 1.84, (d) 2.24, (e) 3.62, (f) 4.6, (g) 5.48, (h) 6.33, (i) 7.5, and (j) 12.4 seconds after exposure to the 120 KeV electron beam, the scale bars are 1 µm. 110
7.4 Time evolution of particle size under the influence of TEM. 111
7.5 TEM pictures of a single hollow particle with different tilting angles, (a) 0, (b) 10, and (c) 30 degrees. (d) Side view of a hollow microbubble. 112
7.6 Size distribution for particles before and after exposure to electron beam. 113
7.7 Transmission electron micrographs and FTIR of plasma polymerized toluene particles: (a) before exposure to e-beam, (b) after exposure to e-beam, and (c) formed at RF power of 20 W. 114
7.8 Transmission electron micrographs of a toluene plasma polymerized particle exposed to (a) argon-ion laser working at 100 mW (b) and argon-ion laser working at 200 mW. 115
7.9 Affect of temperature on toluene plasma polymerized particles. Transmission electron micrographs of the particles at (a) at 100 °C, (b) 200 °C, (c) 250 °C, and (d) 300 °C. 116
7.10 Experimental data for different particles with initial radius of $R_1$ and final radius of $R_2$ are shown with open circles and the solid line shows the fitted line, which is in good agreement with Equation 7.2. 120

A.1 Schematic of constant output atomizer. 133
B.1 Schematic of the core-shell. 135
B.2 Spherical substrate coated with plasma polymer 136
List of Tables

3.1 Summary of Results ................................................. 51
4.1 Solvents Used for Preparing the Colloidal Suspensions ........ 59
6.1 Enthalpy of Combustion for Coated and Uncoated Aluminum Par-
ticles ................................................................. 101
7.1 Carbon-Hydrogen Ratios of Plasma Polymerized Toluene ....... 117
Acknowledgments

During the past five years, I have learned how to properly approach problems in a thoughtful and systematic manner. It was not possible without Dr. Matsoukas who always showed me the right path and taught me the great value of learning from my failures. Themis is a great advisor, a kind person, and Penn State students always know him as a humble teacher. In the second year of my graduate school while we were struggling with the experiments, he gave me one great advice that always helped me through my PhD. He said: “Anaram, be patient and think about the solution. You cannot solve a PhD project without failing, you will learn from that”. He has influenced my personal development as both a teacher and a researcher. I hope one day I can continue my professional life as he taught me. I also thank my committee members, Dr. Joan Redwing, Dr. Robert Rioux, and Dr. Darrell Velegol for their encouragement and advice throughout my research.

I had a great opportunity to start my project in Dr. Matsoukas group with Dr. Carl Marshall. Carl always supported me and I enjoyed working with him. Saba Lotfizadeh also joined Dr. Matsoukas lab in 2011 and it was one of my happiest time during my PhD project working with her. I also enjoyed working with a
number of undergraduate students in the lab. Hassan Aziz AlJama, Tulasi Kolan- dra, Srinath Yelamarty, and Andrew Ferguson helped me in the lab for several semesters. Working and studying in Fenske was really enjoyable for me. During the first semester I found my best friends, Maria Antonieta Sanchez Farran and Laura Mely Ramirez, and since then they have always supported me with love and passion. I also would like to thank Dr. Mahsa Rohani, Dr. Erik Hsiao, Jason Binz, Kiarash Vakhshoori, and Shahrzad Yazdi for their help and support. I also acknowledge the members of Dr. Velegol, Dr. Zydney and Dr. Kim group for sharing their experimental instruments and their laboratory equipments.

Don Lucas, Laurinda Benner, Sue Ellen Bainbridge, and Mary Jane Smith have been wonderful and helpful and made Penn State a great experience for me. Technical and administrative staff in Material Research Lab (MRL) provided a nice environment for performing experiments and Joe Kulik, Trevor Clark, Bangzhi Liu, Maria Klimkiewicz, and Julie Anderson suggested helpful discussion sessions during my work in MRL. I would also like to thank Dr. Borhan for his kind support during these five years.

My father, Mehran Shahravan, and my mother, Parinaz Yazdani, always taught me to enjoy my life. They always encouraged me to learn more and provided everything for me to get through all the obstacles of my life. Their passion and love always keep me going. My sister, Azadeh Shahravan, helped me to find my interest in chemical engineering. As my older sister, she always took care of me and encouraged me to achieve my dreams.
Most importantly, I must thank Shirzad, my husband, for his love and support. Knowing that he would always help me during this journey, made me enjoy every day of my life. I am really happy to start the next chapter of my life with him.
Chapter 1

Introduction

Surface modification and functionalization is highly required for improving physical and chemical properties of nanoparticles (e.g. wear, corrosion resistance, biocompatibility, optical and electrical/electronic properties) [4]. Attaching organic groups or inorganic materials on the surface of nanoparticles influences their interactions with the surrounding environment. Although surface modification changes surface properties, it does not affect the bulk material. Plasma enhanced chemical vapor deposition (PECVD), among different coating techniques, is a unique modification process in which deposition of polymeric films changes hydrophobic properties, corrosion rate, and permeability of the substrate. The concept of forming polymeric materials under the influence of plasma is recognized as plasma polymerization [5]. Plasma polymers are basically cross-linked units of amorphous hydrogenated carbon. Formation of solid amorphous hydrogenated carbons in plasma has been studied vastly in order to use them as dielectric materials for microcapacitors [6–8], composite materials [9], protective coatings [10,11], and also in biomedical applications [12,13]. Plasma deposition, although a well-established technology for wafers and micron-sized substrates, has not been suc-
cessfully adapted to the surface of nanoparticles. In this chapter, the important role of nanoparticles for different applications and the reasons that their surfaces need modification are addressed. Then, the plasma deposition process used for surface modification of nanoparticles is discussed. Some specific properties of plasma deposited coatings are highlighted for encapsulation and corrosion protection applications. Their compatibility with another phase is also studied for nanoparticle stabilization in different liquids. Finally, the conditions for formation of nanoparticles instead of films in plasma are discussed. At the end of this Chapter outline of this dissertation is provided which explains the main goals of this work.

1.1 Nanoparticles

Submicron and nano-sized materials have opened up new possibilities in variety of scientific and industrial endeavors. Nanometer-sized particles have unique electronic, optical, and structural properties which are different from individual molecules or bulk solids. Application of nanoparticles is beyond the scope of this work, therefore we just focus on their advantages for our field of study.

Nanoparticles have received a great attention for encapsulation, drug delivery, and nanofluid applications. Due to high material loading efficiency for variable routes of administration (inhalation and oral application), and sustained and controlled release of loaded materials, they have been considered as a great tool for encapsulation of drugs. Although drug discovery rapidly introduces large number of novel therapeutics, drug targeting and their gradual delivery is limited by the boundary of medical agents that deliver drugs to the right organs. Consequently, a considerable interest has been focused on potential candidates specially
on nanoparticles to overcome some delivery challenges. High surface-to-volume ratio and small size of nanoparticles provide more active area to encapsulate materials. Nanosizing drugs instead of delivering in large quantities of their bulk counterpart, provides a better dissolution (almost 40%) [14]. Since nanoparticles do not aggregate in the blood or settle in the flow of air due to their weight, they are an effective carrier to deliver materials to the target organ. The current focus of drug delivery using nanoparticles as their main tool is for cancer therapeutics [15] and also in neuroscience for tumor therapeutics [16]. Nanoparticles loaded with therapeutic genes, target into malignant cells and gradually release specific amount of chemotherapeutic agents without intervening healthy cells. For brain tumors nanoparticles loaded with small molecules can cross the blood brain barrier which is impossible for larger drug carriers.

Another application for nanoparticles which was examined in this dissertation is using suspended nanoparticles in different solvents, polar and non-polar, as nanofluids. Colloidal suspensions in which the nanoparticle diameter is less than 100 nm that are used for heat transfer applications are called nanofluids [17]. These suspensions have been used as heat exchanger fluids because they show a better thermal conductivity compared to their base fluid [17,18]. Although dispersion of micron-sized particles also improves thermal conductivity of liquids, nanoparticles have great advantages due to their small size. Particles with diameter larger than 100 nm settle down faster, cause clogging in heat exchanger channels, and also dropping the pressure along the fluid flow. But dispersing nanoparticles in solvents also requires stabilization in polar and non-polar solvents which can be achieved by surface modification.

Using metal nanoparticles, especially aluminum, as an additive to explosive
materials is another application for nanoparticles. Due to aluminum high relative heat of oxide formation, mixing energetics and explosives with this metal increase energy output of combustion [19]. In addition, numerous investigations show that melting of aluminum particles with diameter less than 100 nm occurs in very low temperatures (800°C) while, for micron size particles the melting point is around 2000°C [20]. On the other hand, decreasing aluminum particle size causes reduction in aluminum content of each particle due to the spontaneous oxide formation on aluminum surface. For example, an aluminum particle with 500 nm radius has only 5 nm of aluminum oxide on its surface which occupies only 4% on its total weight. But for an Al nanoparticle with a radius of 50 nm, the oxide partial weigh is almost 30% of the overall aluminum weight. Therefore for the aluminum nanoparticles with no surface protection against oxidation, most of the aluminum content will be consumed over time.

Corrosion resistivity, thermal, mechanical stability, and permeability properties of nanoparticles require modification for all of the applications mentioned above. For drug delivery applications and sustained release, a stable drug carrier is needed which can be synthesized by incorporation of both hydrophobic and hydrophilic materials [21] on their surface. To alter stability properties of nanoparticles for nanofluid applications, modification techniques should be utilized to tune surface properties of particles to be adaptive to the new environment of fluids. Since inorganic nanoparticles aggregate in organic liquids, organic functional groups grafted to their surfaces improve nanoparticles dispersion and compatibility with organic environment. Finally, for aluminum nanoparticles depositing a thin layer of passivating coating is required to prevent formation of aluminum oxide on their surfaces.

To conserve initial properties of nanoparticles (e.g. thermal, electrical, and
optical) and achieve unattainable properties that the nanoparticle bulk materials need, surface modification techniques have been used. Coating techniques deposit a thin film of new materials through two different processes, chemical and physical deposition, on the surface of nanoparticles. Depending on the phase of the film forming material which may be solid, liquid, vapor, or gas, the deposition process can be liquid or gas phase coating [22]. Layer-by-layer (LBL) assembly, chemical deposition, self-assembly, chemical adsorption on surface layer, and sol-gel process are the most common deposition techniques that occur in wet environments [23, 24]. In liquid phase deposition, formation of core-shell structures composed of different materials is achievable. Polymeric and inorganic shells have been deposited on organic, inorganic and polymeric cores [23]. Although most of these approaches in liquid phase have been developed for micro-particle colloidal systems, many efforts have led to some strategies to coat nano-sized particles. On the other hand, chemical vapor deposition (CVD) in dry state has not been well adapted for nanoparticle coating although it is a well-understood method for large substrate deposition and nanostructure fabrication [25]. Some CVD techniques have used fluidized bed or rotating shaken reactors and have successfully coated powders and micro-particles [26–28]. Among CVD techniques, plasma deposition is a suitable technique to coat fine nano-sized particles. Plasma deposition has some distinctive advantages such as its ability to expose nanoparticle surface to the reactive environment of plasma in order to coat them uniformly. Previously, it has been reported that particles become charged in plasma systems and get trapped [29]. Trapping leads to hover particles in the plasma reactor. Therefore, trapping is a tool to fluidize particles in the plasma system. Trapped particles react with active gas molecules and ions, resulting in solid thin film formation on
their surfaces. Another advantage of using plasma systems for nanoparticle coating is their great control over the thickness of the film while producing a uniform coating. The main focus of this work was to develop a plasma deposition method for coating nanoparticles. In the following section the mechanism of plasma enhanced chemical vapor deposition is discussed.

1.2 Plasma Enhanced Chemical Vapor Deposition

Plasma enhanced chemical vapor deposition (PECVD) is a chemical deposition process that occurs under the influence of a plasma (partially ionized gas). The plasma forms using a DC discharge or a radio frequency (RF) generator at low pressures (50-1000 mTorr). Low-pressure plasmas are not at equilibrium condition which means the number of ions and electrons are not equal to the number of gas molecules. Although the number of ions and electrons are almost the same, their properties are completely different. Discharges with low-pressure are characterized by a very low temperature for ions, room and slightly above room temperature, and high electron temperature, 11,604 K to 100,000 K, while the overall temperature of the plasma stays between 30\degree C to 300\degree C [30]. The process temperature of a PECVD reaction compared to its equivalent non-plasma CVD is much closer to room temperature. For example, the temperature of the PECVD reaction in order to deposit silicon nitride in integrated circuit fabrication is around 300\degree C while the CVD temperature for the same process is close to 900\degree C. Therefore, PECVD is a great replacement for CVD reaction for sensitive materials to high temperature.

Because of the high temperature of electrons and non-equilibrium condition of
low-pressure plasmas, electrons collide with gas molecules and produce free radicals and excite monomer molecules. Surface of substrates in PECVD reactors absorb free radicals leading to a smooth and high-quality film growth. Amorphous silicon, amorphous hydrogenated carbon, and amorphous fluorocarbon plasma polymers are the common solid thin-films that form in PECVD systems. Amorphous silicon (α-Si) deposition is a well-known process that has application for thin-film transistors in flat panel displays [31], direct-line contact sensors, and solar cells [32]. Silane (SiH$_4$) is the main reactant that forms the glow discharge with a mixture of hydrogen or argon. Silane glow discharge and the mechanism of a-Si thin film growth has been experimentally studied and modeled using Monte Carlo simulation [32,33]. Experimental and modeling results show that silane molecules collide with excited electrons and 100 reactions take place. Some significant products of these reactions are radicals of SiH$_3$ and SiH$_2$ and different ions (e.g. SiH$_3^-$, SiH$_2^-$, SiH$_3^+$, and SiH$_2^+$). SiH$_3$ and SiH$_2$ radicals can attach themselves to the surface and thin-film grows by producing active and passive sites. Passive sites are those chain containing hydrogen or silicon atoms at all four bonds but active sites have dangling bonds. Dangling bonds create bonds with other radicals, leading thin film to grow. At the same time, ions collide with passivated film and create active sites that make bonding with other radicals. Other possible reaction is diffusion of SiH$_3$ radicals along the thin film and bonding with remaining active sites in the lattice and filling the film empty areas and roughness [32]. A similar approach has been used for predicting the desposition mechanism of silicon dioxide [32], titanium dioxide [34], carbon [35], and hydrogenated carbon films [36]. Deposition of amorphous hydrogenated carbon (a-C:H) and fluorocarbon films have attracted attention among PECVD processes because of their wear resistance, low friction
coefficient, and high hardness [37]. A great opportunity stands out for improving a-C:H properties by tuning some parameters during the deposition process. Many characteristic of thin film such as hydrophobicity and surface energy also change by varying the precursor materials. And since any hydrocarbon that forms gas or vapor reacts in plasma systems, PECVD of α-C:H provides a wide range of application and introduces new type of materials that can be utilized in material science and technology.

1.2.1 Plasma Polymerization

Plasma polymerization is a PECVD process when organic materials are used as the reaction precursor. Formation of amorphous carbon-based materials under the influence of plasma is referred to as plasma polymerization process. This terminology was first introduced by Linder and Davis [38] in 1930. Later in 1960, Goodman [5] used polymerization term for formation of solid materials in glow discharge using organic materials for the first time. A great number of research studies focused on the new materials formed in the glow discharge in the field of polymerization in 1970s [39]. Since 1980 some basic studies were done in molecular level to analyze the concept of polymerized materials formation in plasma. Since the new solid materials formed in glow discharges are different from conventional polymers which are composed of repeating molecule structural units, we should not consider plasma polymers as conventional polymers. Not only is their structure irregular, but also they have different chemical and physical properties compared to conventional polymers.

A plasma polymer is a highly cross-linked and highly branched solid that forms under the influence of plasma. Plasma polymers, instead of having a regular re-
peating unit, have short chains that are randomly branched as shown in Figure 1.1. One of the most important characteristics of plasma polymer thin-films is their great resistance to most corrosive chemicals and also their strong adhesion to substrate materials [2].

![High-density polyethylene (HDPE) and Hypothetical structure of a hydrocarbon plasma polymer](image)

Figure 1.1: Molecular structure of polyethylene (conventional polymer), and hypothetical structure of a hydrocarbon plasma polymer [1].

Since the reaction of forming solid thin films from hydrocarbons in plasma systems is a PECVD reaction, it is typically carried out at low temperature and low pressure in the gas phase. Due to the low pressure of the system, reacting gases in plasma are considered as ideal gas in which classical kinetic theories can predict their behavior. According to the ideal gas behavior and kinetic theory, molecules move with a velocity that depends on their temperature and their molecular weight. Due to the molecule collisions, a primary electron forms and by using an electrical fields imposed to the system, the electron will respond due to Newton’s law. Elastic or inelastic collisions occur due to the bombardment between electrons and molecules. Inelastic collisions may excite molecules to a higher level of energy or ionize gas molecules. Ionization is the most important step in plasma polymerization process which provides enough energy for organic gas molecule or nobel gas...
molecule dissociation and excitation. Free electrons that carry high-energy (higher than 10 eV), ionize gas molecules that require 13-25 eV for ionization. Ionized gas molecules of inert gas (e.g. Ar, O$_2$, and He) and organic molecules provide a suitable environment for radical formation. Free radicals are the most important species in plasma that play an important role in polymeric material formation. Figure 1.2 illustrates the polymer formation mechanism and the fast step-growth of a monomer, M, which was discussed by Yasuda [2]. The original molecule of the organic monomer or any product of dissociation process (e.g. hydrogen, fluorine, or chlorine) are represented by $M_i$. $M\cdot$ refers to activated species, radicals, and $M\cdot\cdot$ represents difunctional activated species that are capable of participating in polymerization reaction. Cycle I and cycle II are the main reactions in the rapid step-growth process that produce mono-functional or difunctional species. Some of the activated molecules stay in the polymer structure even after the end of the polymerization. Free radicals trapped in plasma polymer are capable of partici-

![Figure 1.2: Schematic of entire step-growth mechanism of plasma polymerization [2].](image)

Figure 1.2: Schematic of entire step-growth mechanism of plasma polymerization [2].
pating in chain-growth reactions with free radicals in the bulk of plasma. Different models are proposed to explain the process of plasma polymerization for different organic materials. Computational modeling and experimental results try to understand the initiation process, growth of polymers, and termination step based on all the possible ions and radicals formation. Since each organic material has different chemical bonding in its structure, predicting the growth process is unique for every single monomer. Denaro et. al [40] proposed a model for plasma polymerization of styrene for the first time. They explained the initiation process of radical formation and chain-growth through reaction of free radicals in the plasma polymer while their proposed model for rate of reaction had a good agreement with experimental results. Since 1968 when Denaro et al. proposed a model for predicting the plasma polymerization process in order to determine rate of the reaction, many experimental [41] and modeling [36] studies have been done which support chemical kinetics schemes employed for the description of the reaction in the plasma. All models and experiments predict formation of highly branched and cross-linked organic amorphous solids also known as "amorphous hydrogenated carbon" materials.

1.3 Characteristics of Plasma Polymer Films

The primary advantage of utilizing plasma polymerized materials to coat particles and substrates, is their unique physical and chemical properties (e.g. adhesion, permeability, surface energy, electrical properties, etc.). The general characteristics of coatings depend on the chemical properties of the organic precursor and also the condition of the reaction such as the pressure of the reactor, reactor configuration,
flow rate of gas reactant, and power of the generator. As explained above, free radicals have an important role in formation of the thin-film and in its structure. Depending on the molecular bonding and functional groups of the initial monomer, the mechanism of solid coating formation is different because each of the cycles (cycle I or II) shown in Figure 1.2 that affects the process of radical formation will be different. If monomer tends to follow cycle II, more free radicals will form in the plasma polymer. Free radical concentration affects the coating network structure and morphology and causes coatings show different properties. For instance, solid plasma polymer films with high concentration of radicals have low permeability to gas molecules and have very branched molecular network. Some properties of plasma polymers regardless of the starting reactant is similar. For example, typical coatings are adhesive to the surface, insoluble in most of the solvents, inert in chemical reactions, and thermally stable in temperature lower than 200°C. Many studies and developments of plasma polymerized thin films were due to their electrical properties. They have been also used in insulating films, thin-film capacitors, and protective coating for electrical devices on flat substrate [42]. Here, the focus of the work is on permeability, hydrophobicity, and passivating properties of plasma polymer thin films on the surface of nanoparticles and nanopowders.

1.3.1 Permeability and Encapsulation Properties of Amorphous Hydrogenated Carbon Films

The permeation of small molecules into amorphous hydrogenated carbon (a-C:H) films occurs under the chemical potential gradient of the permeant through the thin film. Diffusion in (a-C:H) films due to high degree of cross-linking and large-
scale segmental mobility [2] is extremely low. One advantage of using thin layers with low diffusivity is to decrease membrane permeability [43]. Even in gas phase process, depositing plasma polymerized coating on membranes changes the permeability of different gas molecules. For example, the ratio of $O_2$ gas pressure to $N_2$ gas pressure ($P_{O_2}/P_{N_2}$) varies by coating membrane which can lead to some applications for separation of gas molecules with different sizes [44]. Due to the low permeation in thin layer of plasma polymers, they can be utilized for synthesizing a barrier for controlled release and drug delivery. In Chapter 3, the process of employing a-C:H film for drug delivery applications based on their unique permeability properties is discussed.

1.3.2 Hydrophobicity of Amorphous Hydrogenated Carbon and Fluorocarbon Thin-Films

Chemical properties of the monomer precursor affects the surface energy of the final coating synthesized in the plasma systems. High surface energy results in hydrophilic surfaces and to obtain hydrophilic coatings, polar solvents are used as the monomer precursor in plasma polymerization process [45, 46]. Polar organic monomers have a hydrophilic chemical nature and the plasma polymer formed from these precursors show the same properties. The most challenging problem for using polar monomers is their high boiling point which makes the vapor delivering process difficult. On the other hand, saturated hydrocarbons [47] and perfluorocarbon [48, 49] liquids are not miscible with water and perfluorocarbon are even lipophobic. They preserve these properties when they react in plasma and form hydrophobic films. Experimental and modeling studies explain the mechanism of
producing hydrophobic surfaces [50]. Organic material moieties with hydrophobic coating orient toward the air and the hydrophilic part attaches to the substrate. Hydrophilic, hydrophobic, and super-hydrophobic surfaces are obtained in plasma systems by choosing proper precursors from polar, non-polar, and perfluorocarbon organic material groups [51].

1.3.3 Passivating Properties of Amorphous Hydrogenated Carbon Films

An impermeable shell passivates substrate and particle surfaces by deposition of a thick shell or using a precursor that produces highly branched thin-film. Therefore, plasma polymerized thin films show remarkable application for producing corrosion resistance coating due to their limited permeation properties. Klages et. al. [52] have discussed corrosion protection properties of amorphous hydrogenated silicon carbon (a-SiC:H) films. Since corrosion of metals typically requires oxygen, ions, and water, a protective shell provides an impermeable barrier or a slow diffusion in its structure. Diffusion coefficient of water and oxygen in plasma polymers is in the order of $0.1 \times 10^{-9} - 10 \times 10^{-9}$ [52] which is not a very slow diffusion process. Hence, depositing a hydrophobic cross-linked coating blocks permeation of water and oxygen while having very limited permeability to other molecules. Producing a shell with very low diffusivity also serves as a good protective barrier. It is shown in Chapter 3 and 6 that deposited plasma polymers have a very low diffusion coefficient, which makes them a good candidate for surface protection.
1.4 Nanoparticle Fabrication in Plasma

Plasma deposition has been widely used in different technologies as discussed earlier, due to its great flexibility to produce robust, thin and uniform coatings. Plasma parameters such as reactor pressure, precursor flow rate, and RF generator power, control formation of the thin-film. There is a region in plasma systems that microelectronic technologies avoid, where particles form in plasma. Particles in plasma or so-called dusty plasmas are not favorable for most of coating technologies and many studies have been developed to determine regions that they may be formed [3,53]. Figure 1.3 shows one example of a phase diagram in a capacitively coupled RF discharge at 100 W [3]. As illustrated in this figure depending on the reactor pressure and the precursor flow rate, formation of film, particles, or mixture of film and particles are possible. Formation of powders and their growth follow an entirely different growth mechanism compared to plasma polymer films. Particles form in a relative small volume and high concentration of plasma. Therefore, reactive species diffuse out from the volume of the plasma, nucleate and form small particles. In this situation even if deposition and growth occurs, it will happen on the surface of particles causing growth of particle diameters. Formation of particles is more favorable at the beginning of the plasma reaction when monomer pressure is high and sufficient power is delivered to the gas molecules. But continuing the plasma reaction provides a suitable condition for film formation and leads to powder and film synthesis at the same time.

In spite of all the problems that thin-film manufacturing is trying to solve due to particle formation, other technologies may take advantage of this opportunity. These carbon-based nanoparticles have application in biomedicine, nanoelectron-
ics, and nanofluids [54]. In fact, based on the applications of nanoparticles in different fields some studies focus on increasing probability of powder formation.

1.5 Research Goals

In this dissertation, we attempt to answer a few important questions: Can we uniformly coat nanoparticles and nanopowders by using plasma deposition process? Will the deposited coating be permeable to small solute molecules? Can we deposit thin-films with different hydrophobic properties? Further, are these coatings hydrophobic enough to protect nanoparticles against humidity? And if they are hydrophobic, can we control their properties by changing the precursor
of the plasma deposition reaction? And lastly, can we control the parameters in the plasma deposition process (e.g. pressure, precursor flow rate, radio frequency power) to understand formation of solid thin-films and unstable materials in the plasma?

In examining these questions, we explore the following research goals:
1) Fabricate a thin-film in an isopropyl alcohol plasma to encapsulate silica and potassium chloride.
2) Coat silica and copper oxide particles with isopropyl alcohol, toluene, and perfluorodecalin to tune wetting properties of their surfaces.
3) Suspend hydrophobic particles in non-polar solvents.
4) Coat aluminum nanoparticles to protect them against humidity and oxidation.
5) Explore the parameters for plasma reaction process to form novel materials that are sensitive to temperature shift, laser, and electron-beam.

The main objective of this work is to modify surface properties of nanoparticles in order to use them for controlled release and drug delivery, nanofluid, and metallized fuels and explosives applications.

1.6 Dissertation Outline

Chapter 2 reviews experimental methods and the materials that were used in different chapters of this dissertation. Experimental set-ups are designed and made at the Pennsylvania State University and the process of operating each system is explained in this chapter. Additional information on the materials and experimental process that was unique to that particular work is provided in the beginning of each chapter.
Chapter 3 presents experimental result of coated nanoparticles and nanopowders in an isopropyl alcohol (IPA) discharge. Radial uniformity of deposited plasma polymer coating for very small nanopowders (less than 200 nm) is tested. The main focus of this chapter is studying IPA plasma polymer coating permeability and encapsulation properties which is determined by coating silica nanoparticles and KCl nanopowders. The permeability of the shell is determined by monitoring the concentration of core material in a proper solvent which dissolves it. Although plasma polymerized coating is highly cross-linked, it is permeable to small molecules. The behavior of the core dissolution which represents the profile release of core materials, is modeled using Fick’s diffusion law. Based on this model, the diffusion coefficient of the shell is determined. Due to the slow permeation of the shell deposited by plasma polymers, this technique shows promising results for long term encapsulations of nanoparticles for drug delivery and controlled release applications. The final result of nanoparticle coating and dissolving the core material is the formation of hollow particles. We explain in this chapter the process for controlling the core diameter, shell thickness, and encapsulation properties of the hollow particles that were fabricated using the PECVD process.

Chapter 4 introduces new organic precursors for plasma deposition process for controlling the hydrophobicity of nanoparticle surfaces. Isopropyl alcohol, toluene, and perfluorodecalin are the main reactants that change hydrophilic properties of nanoparticles after they are deposited on their surfaces. Wettability properties of thin-films is determined using water contact angle measurements. Since hydrophobic properties of coated particles for each coating is different, particles tend to mix with different solvents ranging from polar to slightly polar and non-polar solvents. Coatings preserve the chemical and physical properties of the original
liquid precursor. Polar solvents form hydrophilic coatings, non-polar solvents produce hydrophobic coatings and lipophobic liquids form a plasma polymer thin-film which are superhydrophobic while showing lipophobic properties as well. The results from dispersing coating particles in different solvents demonstrates the great potential of this method for different applications such as nanofluids.

Chapter 5 gives an analysis of colloidal suspensions as nanofluids that are used as heat transfer liquids. It has been shown that suspending particles in solvents improves thermal conductivity of the base fluid. Thermal conductivity of stable suspensions were measured and were compared to the models that predicts nanofluid thermal conductivity. The thermal conductivity improvement observed for suspension of CuO in oil-based solvents with 1 vol% is up to 40%. The novelty of our method is its ability to produce stable suspensions in refrigerant-base liquids which has not been previously done with any deposition process.

Chapter 6 examines the passivating characteristics of hydrophobic plasma polymerized coatings. Aluminum nanoparticles are chosen as the core materials due to their application as an additive to energetics materials. Aluminum nanoparticles release large amount of energy since their energy density for oxidation process is -7.4 kcal/g. The most challenging problem with aluminum particles is the oxide layer that forms on the surface of particles after being exposed to atmosphere and humidity. Since the oxide layer weight can occupy more than 60% of the nanoparticle weight, formation of this layer decreases the amount of active materials. Therefore, plasma coating is utilized to passivate their surfaces. Hydrophobic coatings that were explained in chapter 4, are synthesized on Al nanoparticles and the amount of oxide layer is measured for uncoated and coated particles. The results show less aluminum oxide is formed for coated particles compared to the
uncoated ones. In addition, deposition of coating also improves the enthalpy of combustion of Al nanoparticles at elevated temperatures.

In chapter 7 a one-step process for formation of hollow particle that grows like a bubble in a plasma system is explained. First, particles are formed in plasma system using a toluene discharge. Then, they form a microbubble after exposure to an external energy. External stimuli such as electron beam, laser, and temperature shift affect the network of the liquid (oily) plasma polymer. Through a chemical reaction, liquid-like materials produce a cross-linked and branched solid and release gas molecules. This chapter discusses the potential applications for "smart particles" that respond to external stimuli and also their role for other applications that were discussed in chapter 3 for hollow particles.

Chapter 8 summarizes the dissertation and gives detailed recommendations for future works. The focus of this chapter is on the design of a new system, substrate surface passivation, preparation of anti-fog and anti-ice coatings, synthesis of microbubbles, and formation of hollow particles.
Experimental Procedure

This chapter describes the experimental setup that are common within different chapters of this dissertation. However, more information is provided in a separate section within the text of that chapter.

2.1 Construction of the Experimental Setup

2.1.1 Different Configurations of the Reactors

Plasma deposition and nanoparticle coating are examined in a capacitively coupled plasma (CCP) system. Two typical configurations for plasma enhanced chemical vapor deposition (PECVD) generated by a radio frequency (RF) system have been developed. In the first configuration, parallel electrodes are placed inside of a reactor and are capacitively charged. In the second one, plasma is formed by inductively couple plasma using a coil electrode which goes around a tubular reactor. A combination of these two common configurations is used in this work by employing two electrodes outside of a tubular reactor to generate capacitively
coupled plasma. Two homemade reactors were designed which are essentially glass cylinders with one inlet and one outlet. Two glass reactors are defined by their configuration which is either horizontal or vertical. The vertical reactor, Figure 2.1 (a), is a pyrex tube with inner diameter of 1 inch and length of 10 inches. The pyrex cylinders are made in a glass shop at the Pennsylvania State University. In order to connect the glass reactor to the gas inlet and to the vacuum system two glass-to-metal adapters were purchased from A&N corporation. These adapters facilitate the attachment of glass tube to metal pipe of gas inlet and high vacuum system. The A&N glass adapters have a flange on their metal side which can be easily sealed with a wing nut aluminum clamp purchased from the same vendor. Fittings and flexible tubings were obtained from Swagelok. The OD of inlet pipings is 1/4 in and OD of stainless steel outlet flexible tubing is 1 in. A flange sealing process was followed for each connection point by placing an O-ring between two flanges and fastening the connection using an aluminum clamp.

Figure 2.1: Description of the (a) horizontal tubular reactor and (b) vertical reactor.
2.1.2 Vacuum System

The main part of the vacuum system is an Edwards RV rotary pump. The RV pumps are easy to use and maintain and the only procedure that should be followed is checking the pump oil and controlling the level of this liquid in the pump. The pump pressure is controlled and monitored by an active thermocouple gauge (ACT-E) equipped with a pressure display. The rotary pump has also an oil mist filter to trap mist and odors of oil before exhaust gases travel to a fumed hood. In order to have a clean pumping system and prevent the back-migration of rotary pump oil vapor into the pump, an Edwards FL20K Foreline trap is used. O-rings and aluminum clamp are also used for connecting and sealing mist and oil trap. An stainless steel liquid nitrogen (LN) trap is installed between the rotary pump and the reactor. Cold LN trap captures unreacted hydrocarbon vapors from the reactor discharge and allow the system’s gaseous exhaust to be clean. Nanoparticles may also blow off from the reactor but will be collected on the cold surface of the LN trap as well. For a complete process to separate nanoparticles from the reactor exhaust, particle filters are place inside of the pipe that connects the reactor to the LN trap. More detailed information regarding the arrangements of different parts in the vacuum system is shown in Figure 2.2.

2.1.3 Flow Controllers

Two mass flow controllers (Edwards 825) are used to measure and control the flow of argon and oxygen. Each controller is designed for a specific gas and controls in the range of 0 to 500 sccm. A digital flow display and controller (Edwards Type 1605) provides power, flow reference level, and valve control for the two
Figure 2.2: A schematic of the plasma enhanced chemical vapor deposition set-up used for the present work.

mass flow controllers that are connected to the argon and oxygen cylinders. Since variety of hydrocarbons are used for plasma deposition process, no unique mass flow controller could be used. Therefore, mass flow is monitored by controlling the temperature of a water bath and also using a critical orifice between hydrocarbon flask and the glass reactor. Water bath temperature controls the rate of evaporation hence can be calculated for each liquid to define a proper flow rate for each experiment. The only challenging draw back of evaporating liquid materials is their sudden effect on reactor pressure. The critical orifice was used to overcome this problem which is a simple solution to reduce the flow of materials. Critical orifice reduces the diameter of the pipe from 1/4 in to 0.0074 in and the change in the size of the gas pathway reduces the number of gas molecules that pass through the pipe (shown in Figure2.2). Reducing the size of the pathway maintains a constant flow when pressure suddenly increases. The critical orifice was made by drilling a small hole (0.0074 in) in a seal face fitting that connects the outlet pipe from precursor flask to the inlet of the glass reactor.
2.1.4 Plasma Power System

The plasma processing reactor contains two aluminum electrodes that are shown in Figure 2.2. Electrodes are placed 1 inch apart from each other and one electrode is connected to an ENI ACG-3XL radio frequency (RF) power generator. This generator delivers RF power up to 300 W at frequency of 13.56 MHz. RF generator is connected through RF cables to a matching network. When impedance is mismatched, the ENI MW-5D matching network automatically increase the power dissipation in the discharge to protect the power source.

2.2 Protocol of the System Operation

Although operating the plasma and vacuum system follows a standard procedure, using low pressure reactor requires planning and special precautions. Wearing safety goggles, lab coat, and gloves is recommended for the entire procedure. Depending on the experiment some sample preparation is needed. For some experiments particles are placed inside of the reactor before starting the experiment. Then, the glass reactor is sealed by placing an o-ring between two flanges, one at the end of the glass tube and one at the end of the pipe that is connected to the pump. And finally, the aluminum clamp ring is installed around the flanges and the screw is hand tightened around the clamp.

2.2.1 Preparation of the Vacuum System

First, the liquid nitrogen trap is filled until the surface of the trap become cold. It typically takes 5 minutes. To seal the entire system, the glass liquid flask is connected to the plasma reactor by tightening the plastic nut that connects the
reactor inlet to the liquid flask. After placing the glass flask in a water bath with a controlled temperature, the argon gas flow controller is turned on. Gradually, the gate valve that connects the glass tube to the pump is opened while the pump is working. Performing this step requires appropriate handling because sudden decrease of pressure may cause the particles to be blown away by the flow. As soon as the pressure reaches 200 mTorr, the gate valve should be fully opened.

2.2.2 Operating the Plasma Deposition Process

The aluminum ring around the tubular glass reactor is connected to the radio frequency, RF, generator and the stainless steel clamp is connected to the ground during the plasma deposition process. First the matching network is turned on then the AC line and the RF generator power are switched on. The power should be set at the desirable power. After a specific duration of time (10, 20, or 40 min) the matching network, RF generator, and the AC power goes off respectively. Closing the check valve and turning off the argon flow controller is done right after finishing the plasma operation. Extra precautions adhered when opening the reactor because the pressure is really low.

2.3 Reactor Cleaning

During the plasma deposition process not only particles or wafers become coated but also thin-film deposition occurs on the reactor walls. The coating on the wall surface become thick after each experiment and this remaining residue cover the glass surface of the wall. Since this coating has a very good adhesion to the glass surface, conventional cleaning methods like mechanical and chemical cleaning does
not remove it. Oxygen plasma cleaning is the easiest chemical process for ultra-
cleaning of the reactor. After each experiment and collecting the samples, all the
system operation protocols are followed. For oxygen cleaning, we turn the three-
way ball valve on to connect the oxygen valve to the reactor. The oxygen flow rate
is controlled at 9 sccm and the plasma is operated at 50 W for 5 minutes.

2.4 Materials Characterization Techniques

2.4.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) provides the possibility to image de-
posited films with very small thickness down to angstrom range. Although the
plasma deposited thin-film is amorphous, it is detectable for thickness thicker
than 1 nm. Copper mesh covered with thin layer of carbon are used as the sample
holder. The delicate should be handle with extra caution during the sampling
process. For uncoated samples or hydrophilic coatings, particles are suspended in
isopropyl alcohol with volume concentration less than 0.05% and the TEM grid
is dipped in the suspension. For hydrophobic coated particles, a subtle procedure
is followed. First, particles are mixed with a mixture of water and dodecane and
are fully shaken. After transferring them to a separating funnel, water phase is
separated from the oil phase. Following this procedure separates coated particles
from the uncoated ones. Dodecane part of the sample is transfered to a Petri dish,
then IPA is added to dilute oil. Dodecane blocks the grid surface in the TEM and
makes micrographs seems blurry. Adding IPA causse particles aggregate but since
TEM is a dry-state characterization technique, it also happens to non-aggregated
samples as well. Philips (FEI) EM420T with tungsten emitter accelerated at 120
kV is used for all the images prepared in this dissertation.

### 2.4.2 Scanning Electron Microscopy

Scanning electron microscopy (Hitachi S-3500N and Hitachi S-3000H) is conducted for collecting images from the surface topography and morphology of particles with diameter larger than 200 nm. Field emission scanning electron microscopy (Leo 1530 FESEM) is a high resolution SEM and is used for preparing images from particles specially those with diameter less than 200 nm. Particles are first suspended in proper solvents, IPA or dodecane, depending on their hydrophobic properties and then are spread on the surface of a clean silicon wafer which is cleaned by operating RCA-1 cleaning. After putting one or two droplets of each sample on the surface of wafer, it is placed under a fume hood. After evaporating IPA or dodecane, sample is reading for imaging.

### 2.4.3 Dynamic Light Scattering

Size distribution and average particle size is determined using dynamic light scattering (DLS). For each measurement, particles are placed in a glass tube with volume of 5 ml. In order to prevent multiple scattering, sample concentration should be low therefore, samples with concentration higher than 0.5 vol% are diluted with the base fluid prior to DLS measurements. Since viscosity of the sample is very important for size measurements, base fluid of each sample should be know. This method is proper for monodisperse samples and it is also used to study the sample stability.
2.4.4 Zeta Potential Measurements

To determine the stability of the samples, zeta potential measurements are conducted for polar solvents using Brookhaven ZetaPals instrument. Zeta potential is considered as the electric potential of the interfacial double layer (DL) and its value smaller than 25 mV, negative or positive, show low-charged surfaces in the suspension. Zeta potential indicates the repulsive forces between particles and low-values means that the suspension is not stable enough and particles aggregate gradually.

2.4.5 Thermogravimetric Analysis and Differential Scanning Calorimetry

To analyze thermal behavior of coated samples and plasma polymers, thermogravimetry analysis is conducted in a TA Instruments SDT model 2960 which simultaneously perform differential scanning calorimetry (DSC). For coated samples, dry particles collected in the plasma reactor are incubated in desiccator to prevent adsorption of water and contamination. To conduct TGA on plasma polymers, plasma deposition is performed in the empty reactor and coatings are collected from the reactor wall. The TGA is a very important experiment for determining thermal behavior of aluminum nanoparticles and detail information is provided in Chapter 5 for that specific experiment.

2.4.6 Fourier Transform Infrared Spectroscopy (FTIR)

Information about chemical structure and organic functional groups of plasma polymers is obtained from FTIR (Bruker IFS 66/S FTIR spectrometer) spectra.
For particles suspended in solvents a KBr pellet is soaked in the liquid to collect particles and is dried by argon gas. For collecting IR spectra from plasma polymers, gold and silicon wafers are coated in the plasma reactor under the same condition that particles are coated.

### 2.4.7 Water Contact Angle Measurements

Measuring the contact angle between a sessile droplet and nanoparticle surface is not experimentally possible. Therefore, two strategies can be followed. In the first strategy, a smooth wafer is coated with the same material that particles are coated with. And in the second strategy, a clean and smooth wafer is spin coated with coated particles. Using spin coating requires having a well-dispersed sample in non-aqueous solvents. It is very important to only deposit one layer of coated particles because aggregated particles improves surface hydrophilic properties [55]. After preparing samples following either strategies, a sessile droplet of DI water is placed on the wafer and a CCD camera is used to capture the image. Then the contact angle between droplet and surface can be measured using ImageJ software.

### 2.4.8 Thermal Conductivity Measurements

Transient hot wire (THW) test is a standard method for measuring fluid thermal conductivity. In this method, solvents are placed in a test cell, glass tube, that has a wire at its center. The wire is heated and is considered as a linear heat source with a constant and uniform output. During a specific time the temperature rise in measured for a known length of wire and the thermal conductivity can be derived measuring the change in the temperature. For experiments explained in Chapter 4, thermal conductivity was conducted in the Advanced Cooling Technology that
collaborates with Dr. Matsoukas at the Pennsylvania State University. Each experiment was performed for two runs and in each run six data was collected. Samples are sonicated for 30 minutes prior to each test.
Chapter 3

Encapsulation and Controlled Release from Core-Shell Nanoparticles Fabricated by Plasma Polymerization

The majority of the work presented in this chapter was previously published in the Journal of Nanoparticle Research (Shahravan and Matsoukas, 2012) [56].

3.1 Introduction

Controlled release and encapsulation technology have focused on nano-sized hollow materials because of their high performance in many applications, especially drug delivery due to their high loading capacity [57–60]. Microencapsulation has been studied in both wet and dry state and has been commercialized using fluidized bed technology in Wurster process [61] whereas coating of nano-sized particles or
encapsulation of nanoparticles has been mostly developed in wet environment [62]. Aggregation of dry particles prevents formation of coating around fine particles hence encourage developing new methods for coating nanoparticles and producing nano shells [61].

Encapsulation produces a barrier that isolates the core material from its environment and provides a medium for controlled release of the core. Pharmaceuticals [63–65], cosmetics [66,67], energy storage materials [65,68] and food particles [69,70] are some familiar products that are commonly used in encapsulated form. The encapsulating material is usually polymeric in nature [71–73] although considerable interest has recently focused on silica-based materials [66,74–77]. Encapsulation of micro- and nanoparticles is most often accomplished using the tools of colloid chemistry and sol-gel process under liquid phase processing [24,77] and to a lesser extent by gas-phase processing [65,78]. In the one-step process, the material to be encapsulated serves as the core during encapsulation. Since liquid-based techniques require some degree of chemical compatibility between core material and shell, which is not always present, an alternative process is to encapsulate a sacrificial particle, etch the core material, and load the species of interest in the hollow shell that is formed [24,79]. This technique is severely limited by the amount of the material that is loaded into the hollow carrier, which cannot exceed the solubility of the material of interest in the solvent [80]. Such difficulties can be overcome by gas-phase processing. It has been shown recently that flame deposited silica provides a barrier on the surface of silver nanoparticles to an extent that their toxicity is substantially suppressed [65]. Flame processing, on the other hand, is feasible only with core materials that are stable at flame temperatures.

Here, we report on the feasibility of a plasma based process to deposit an
encapsulating shell on a core particle that can act as a controlled barrier to the release of the core material. Plasma deposited shells appear to have potential application in drug delivery due to their advantages such as chemical stability, low toxicity, and thermal stability [81]. Plasma polymerization is a technique that has the ability to coat micro- and nano-sized particles with shell thickness ranging from one nanometer to several 100 nm [29, 61, 82, 83]. Plasma polymer refers to solid materials formed by the decomposition and subsequent cross linking of organic molecules in a non-equilibrium glow discharge [84]. While they lack the regular structure of a repeating monomeric unit, they consist of an amorphous network of carbon and hydrogen whose degree of cross-linking and permeability depends on the precursor molecule and the deposition conditions. Plasma polymers can be produced by any hydrocarbon that can be brought into the plasma in gaseous form and can be deposited on nearly any type of substrate. They are chemically inert, provide excellent barrier properties, exhibit varying degrees of hydrophobicity, depending on the precursor molecule, and have been shown to be biocompatible [12, 13]. Plasma deposition has not been completely adapted for coating particles. Much research has focused on coating and modification of micron and nano-particles [85–87]. Forming an extremely thin, 1 nm, adherent film is one of the challenging step for coating nanoparticles. PECVD method is a powerful technique while it can easily control the coating thickness to achieve a thin film, 1 nm, without any cracks and roughness. This ultra thin coating can also be deposited on the particles with different size (100-2000 nm) and different materials (e.g., silica, silicon, gold, carbon, and titanium oxide, alumina, copper oxide) [29, 82, 88–90]. Not only PECVD able to coat different substrate but also a wide range of hydrocarbons can be used as plasma polymerization precursor.
In this study, we use a low-pressure radio frequency plasma to deposit thin films onto particles using isopropanol as the organic precursor. This particular precursor has been shown in previous work to form very smooth films that, while hydrophobic, can be suspended in aqueous media, are mechanically stable, and can be deposited on various substrate [29, 91–94]. We demonstrate the controlled deposition of these films on two different substrates, silica and KCl nanoparticles, and report on their permeability characteristics through dissolution studies of the core material.

3.2 Experimental

3.2.1 Materials
Silica particles (diameter of 200±3.5 nm and 1000±1.7) were purchased from Geltech Inc. Potassium chloride (crystals) and sodium acetate (crystals) were obtained from EMD Chemicals Inc. and Sigma-Aldrich respectively. A mixture of compressed argon gas and isopropyl alcohol (99.9% Sigma-Aldrich) was used in all the plasma coating experiments. Hydrofluoric acid (48-51%) was purchased from VWR and deionized water was obtained from a NANOpure Diamond water purification system (Barnstead Thermolyne Corporation, Dubuque, IA) with a resistivity greater than 18 MΩ-cm.

3.2.2 Silica and Potassium Chloride Particle Preparation
To prepare silica particles for the coating experiment, they were washed in ethanol (200 proof pure Koptec) and were dried under the fume hood. After drying, they
were passed through several standard mesh series (US # 100-400) to separate remaining aggregates from the rest of the sample. To synthesize KCl particles, a constant output atomizer (TSI model 3075) was used [95], which generates sub-micron aerosols. Fresh solution of 0.5 M KCl in a flask supplies the material for producing aerosol particles. These particles are then passed through a column of silica gel in order to remove moisture. The powder collected at the end of the dryer was ground and crushed to loose any agglomeration, and then passed through a set of US # 100-400 mesh screens. Appendix A contains more information about the process of preparing silica nanoparticles and KCl nanopowders.

3.2.3 Deposition Technique: PECVD for Synthesis of Core-shell Structure

Thin-film deposition took place in a radio frequency plasma chamber, which was built in our lab. The plasma was formed in a pyrex tube, 1 inch in diameter and 10 inch in length, which was mounted horizontally. After passing uncoated particles through mesh screens, we transferred them to the horizontal tube using a metallic spatula. A magnetic stirrer bar (1.5 mm in diameter and 8 mm in length purchased from VWR) was used to agitated the particles and expose them to the plasma. We place the stirrer inside the reactor on its surface with uncoated particles. After formation of the plasma in the reactor we turned on a magnetic stirrer which was placed underneath the tube as shown in Fig 3.1 to move the stirrer bar and agitate the particles. We have investigated the effect of the stirring speed and have found that if the speed exceeds 100 rpm, the stirrer bar blows the particles off from the place which deposition takes place. As shown in Fig. 3.1, carrier gas and the
precursor were introduced to the reactor at one end and evacuated at the other end of the tube. Argon gas serves to carry isopropanol vapor through a gas bubbler, which is kept in a water bath at a constant temperature \((34 \pm 2) ^\circ C\). The heated bath allows the gas bubbler (25 ml in volume) temperature stays constant thus delivers deposition materials uniformly and constant to the chamber. To connect the other side of the tube to the vacuum system, the glass to metal sealed flange (A&N corporation ISO-QF to Glass Adapter) was designated. After putting the particles inside the chamber, the glass to metal adapter was sealed to the vacuum line by a hinged clamp. The vacuum line is connected to a liquid nitrogen trap and the rotary pump (Edwards RV3) that was operated at 1 mTorr. Using the trap helps to keep the pressure constant by preventing the particles and isopropanol vapor from entering the pump.

![Figure 3.1: Schematic diagram of the experimental set-up used for nanoparticle coating.](image-url)
The reactor was capacitively coupled with a 13.56 MHz radio frequency (RF) generator. RF power of 30 W is applied to a ring-like aluminum electrode which was placed 1 cm apart from the grounded electrode outside of the glass tube. A 0.6 sccm isopropanol flow and 6 sccm Ar flow brought up the pressure to 200 mTorr and was maintained constant. Typical deposition experiments run for 2 to 90 minutes, depending on the desired thickness of the coating.

3.2.4 Dissolution of Core Materials

Hollow particles were synthesized by dissolving the core materials in a proper solvent. The silica core was etched out in a dilute hydrofluoric acid solution (48-51 vol. % solution). After two days, the mixture of dissolved silica, hydrofluoric acid, and hollow shells were centrifuged, followed by 2 washings in water. Hollow particles were separated by centrifugation (30 min at 1163 g) from the solution and the remaining water was gently evaporated in a ducted fume hood. KCl-coated particles were dissolved in deionized water then hollow particles were centrifuged and washed after 6 days. Sampling for transmission electron microscopy (TEM) was performed during and after the core dissolution process.

TEM was performed in a Philips EM420T (operating at 120 kV) in order to reveal the core-shell and hollow structure and to measure the thickness of the shell. The electron microscopy images were obtained on a ZeissSMT 1530 field emission scanning electron microscope (FESEM) and thermogravimetric analysis (TGA) measurement is done by TA Instruments TGA 2050. To measure shell thickness and particle's size, ImageJ software is employed.

The release profile of core is studied by monitoring the dissolution rate of coated KCl particles. We can detect the concentration of dissolved KCl by using
a conductivity meter (Thermo Orion model 105) during the process. Coated KCl particles were stirred vigorously in a glass vial which was kept in a water bath with constant temperature of 25°C. The glass vial was kept capped at constant temperature, and a control solution, maintained under the same conditions, was used to correct for possible evaporation effects.

### 3.3 Results and Discussion

#### 3.3.1 Hollow Particle Size and Morphology

Figure 3.2 shows 200 nm particles (a and b) and 1 µm particles (c) after plasma treatment. For the most part, coatings are deposited with satisfactory radial uniformity, indicating that the magnetic stirrer is quite effective in exposing the majority of particles to the reactive plasma.

![Figure 3.2: TEM images of coated silica particles with diameter of (a),(b) 200 nm, and (c)1000 nm. Coating thickness is 9.3±2.3 nm, 15±4.7 nm, and 12±4.5 nm respectively. Scale bar= 100 nm](image)

The thickness of the film is controlled by the deposition time. We find that the thickness of the coating is a linear function of the deposition time with a deposition
rate of approximately 1 nm/min, as shown in Figure 3.3. This rate is in good agreement to the one reported by Matsoukas and Cao [29], for coatings deposited in particles that are electrostatically trapped in the sheath of a capacitively coupled plasma. The low rate of deposition allows for a fairly precise control of the thickness of the coating in the entire nanometer range.

![Graph showing shell thickness vs. plasma deposition time]

**Figure 3.3:** Shell thickness on the surface of KCl particles exposed to the same plasma for different coating time

Figure 3.4 shows the hollow nanoshells produced from the 200 nm silica. After the treatment in hydrofluoric acid, silica is absent from the interior of the shells. Despite the highly corrosive environment during etching, shells remain intact. The diameter of the hollow center matches the size of silica core, while the average thickness of the shell in this sample is 40 nm. This corresponds to a void fraction of 36%.

Scanning electron microscopy is a very common technique that has been performed to investigate the roughness and morphology of the surface. In this regard we have done FESEM to study surface morphology of hollow particles. Figure 3.5
Figure 3.4: TEM images of hollow particles after etching the silica core with diameter of 200 nm

is an FESEM picture of the same particles that we used to obtain TEM. The exterior surface is smooth and the shells appear solid and robust. FESEM also reveals that not all particles are coated uniformly. The half-shells seen in Fig. 3.6 are characteristic of particles that remain in contact with a surface (reactor wall) during the deposition process and receive a coating only on the side exposed to the plasma. However, we do not observe fragmented shells, or particles with multiple holes that would indicate touching particles whose contact points are inaccessible to the plasma. The presence of open shells is not uncommon in coating/dissolution processes, as has been reported by others in liquid-phase synthesis of hollow nanoparticles [96,97].

To estimate the coating yield as a fraction of the total amount of silica placed in the reactor, we employed a simple separation technique. After the deposition experiments, particles were dispersed in a two phase (water-dodecane) solution
and were vigorously shaken. Coated particles are hydrophobic and preferentially migrate to the oil phase, while uncoated particles are found in the water/oil interface. By this method, the fraction of particles that are coated is approximately 70%.

The thermal analysis of hollow particles were done by using TGA up to 700°C. The main observed weight loss appeared in one stage between 250°C to 550°C, Fig. 3.7 (a), which indicates that the particles are stable below 250°C. In addition to the TGA analysis, particles were collected from a furnace with the same heating rate at different temperatures. TEM picture are taken for these temperatures and as shown in Fig. 3.7 (b), and (c) hollow particles preserve their spherical shapes up to 100°C, and 250°C; but hollow particle surfaces and their sizes undergo some changes. Particles are expanded and their outer diameter changed from 280 nm to 295±5 nm. Expanding did not cause rupture of hollow particles below 250°C only caused roughness on the shell surface but above this temperature cracked and collapsed shells are observed (Fig. 3.7 (d)).

3.3.2 Release Profile of Coated KCl Particles

The successful etching of the silica core is evidence that the shell is permeable to small molecules such as HF and water, which move into the core, and soluble silica, which is transported to the solution. To study the release profile in quantitative terms and avoid the difficulties associated with the handling of hydrofluoric acid solutions, we have used KCl as the core material, which allows us to measure the dissolution profile by measuring the ionic conductivity of the solution as a function of time. The remarkably simple procedure, which is explained in the experimental part, allows us to produce rounded nanoparticles of KCl. Figure 3.8 shows TEM
Figure 3.5: Field emission scanning electron micrograph of hollow particles after etching the silica core and 10 minutes of sonication

images of the coated particles at various stages of dissolution. KCl particles with average diameter size of 110 nm were coated for 40 minutes. The average thickness of coating according to Fig. 3.3 is $40 \pm 10$ nm. After about one hour of dissolution, re-crystallized KCl can be seen outside the particle, though no visible changes are seen in the core material itself. At six hours the core shows visible signs of dissolution and after 6 days the sample consists of only hollow shells with no visible core.

To study the dissolution profile, four samples of coated KCl particles were prepared with average shell thickness of 20, 40, 75 and 95 nm. The average diameter of KCl particles and shell thickness for each sample is shown in table6.1. Figure
3.9 shows the concentration of dissolved KCl in the solution as a function of time. In addition to the four coated samples, a sample of uncoated KCl was measured to serve as control. Uncoated KCl dissolves very rapidly and within 30 s its concentration in solution reaches a constant value that remains unchanged. The release profile through the coated particles is much slower than the control and lasts up to several weeks for the thickest samples. All samples show some common characteristics. The initial release is quite fast and within the first five minutes the concentration of KCl reaches between 35% and 80% of its final value, depending on the thickness of the coating. The rapid release is likely due to partially coated particles, such as those shown in Fig. 3.6. The sample with the thinnest coating (20 nm) shows the maximum initial increase of KCl concentration (70%), while
the thickest sample (95 nm) shows the smallest increase (35%), indicating that prolonged coating decreases the fraction of partially coated particles, as we would expect from the prolonged presence of particles in the plasma and the continuous agitation. After the initial rapid build-up of KCl concentration, the profile switches to a markedly slow release that lasts over a period of several days. Full release is achieved at about 6 days for the thinnest sample (20 nm), and after more than a month for the thickest (95 nm). The point of complete release is defined by the constant value of measured concentration in solution. This concentration is also
calculated by mass balance based on the weighted amount of coated particles and the known mean size of the core. The two values generally agree to within 8%-10% of each other. Therefore, the release rate can be controlled very easily via the thickness of the shell. This is an advantage over the layer-by-layer process, which typically releases the core within hours [63, 74, 98, 99]. While polymer coatings have been reported to increase the release time to several weeks, this could only be achieved with a certain polymer [100]. Our process does not suffer by this limitation. 8%-10% of each other.
Figure 3.9: Effect of shell thickness on the release profile. The inset graph shows the release during the first hour.

### 3.3.3 Analysis of Release Profiles

The standard mathematical model in controlled release is based on the solution of the unsteady-state diffusion equation from a sphere which is explained in Appendix B. The analytical solution derived by Crank [101], Eq. 3.1, is used to determine the diffusion coefficient of various structures and materials such as drug release from core-shell structure [102,103], emulsion gel [104], and spherical biodegradable nanoparticles [105].

Assuming at time zero the solute to be uniformly distributed across a sphere of
radius $R$ and the solution to contain no solute, the amount of solute in the solution at time $t$ is

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{\exp(-n^2D\pi^2t/R^2)}{n^2}, \quad (3.1)$$

where $M_t$ is the cumulative amount of solute released at time $t$, $M_\infty$ is the total amount of solute, and $D$ is the diffusion coefficient of the solute. For large $t$, only the first term of the series is important and the result becomes

$$\frac{M(t)}{M_\infty} = 1 - \frac{6}{\pi^2} \exp(-D\pi^2t/R^2). \quad (3.2)$$
This simpler equation is in very good agreement with the exact result in equation 3.1 for $M_t/M_\infty \geq 0.6$. According to Eq. 3.2, a semilogarithmic graph of $1 - M_t/M_\infty$ should yield a straight line whose slope is proportional to the diffusion coefficient. This plot is shown in Fig. 3.11. The linearized form represents the long-time data well. Interestingly, the fitted lines extrapolate to a common intercept whose value is very close to the predicted value ($6/\pi^2 \approx 0.61$), however this point is slightly into the negative time axis, at $t \approx -1.85$ days. The diffusion coefficient is now calculated from Eq. (3.2) using the radius of the coated particle, which includes the thickness of the shell. The calculated values are of the order of $3 \times 10^{-21}$ m$^2$/s. The diffusion coefficients obtained in this manner are independent of the thickness of
the shell (see inset graph in Fig. 3.9 and also Table (6.1)). The result suggests that the model provides a consistent description of the long-time release and correctly accounts for the resistance of the shell via the size $R$ of the coated particle. The calculated profiles using the fitted values of the diffusion coefficient are shown in Fig. 3.11 and can be seen to provide good description of the experimental data after about 0.5 days from the start of the experiment until full dissolution of the core. The earlier part of the profile cannot be fitted by the model.

Equation (3.1) assumes that the solute is initially uniformly distributed in the matrix through which it must diffuse. This situation is appropriate for diffusion through a hydrogel that is loaded with the solute. In our case, the solvent (water) must first diffuse into the core and dissolve the KCl before the solute permeates the shell. In this respect, Eq. (3.1) is not strictly valid at the initial stage. Additionally, half-coated particles further alter the early release profile. Nonetheless, the very good agreement between model and data after the first half hour, and the agreement in the value of the diffusion coefficient obtained from the four different samples, lends confidence to the conclusion that the diffusion model provides a consistent description of the release profile.

### 3.4 Conclusions

Deposition by plasma polymerization has been shown to be a feasible alternative for encapsulation of nanoparticles. The process offers several advantages: as a dry process, it avoids contamination issues associated with liquid phase deposition; it works quite well with particles of any size, include particles in the low nanometer range; it is capable of producing films from few nm to more than 100 nm in
thickness; it can be applied to any substrate material. We have shown that films are permeable to small molecules and ions (water, soluble silica, $K^+$, $Cl^-$) and that the permeation rate is determined by the thickness of the deposited film, which in turn is controlled directly by the deposition time. One experimental challenge in this process is to maintain the radial uniformity of coatings as the process is scaled up. This is currently under investigation.

Table 3.1: Summary of Results

<table>
<thead>
<tr>
<th>Samples</th>
<th>Core material</th>
<th>Core average size (nm)</th>
<th>Shell average thickness</th>
<th>$D$ ($m^2/s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ - 200</td>
<td>SiO$_2$</td>
<td>200±3.5</td>
<td>15±4.7</td>
<td>–</td>
</tr>
<tr>
<td>SiO$_2$ - 1000</td>
<td>SiO$_2$</td>
<td>1000±1.7</td>
<td>12±4.5</td>
<td>–</td>
</tr>
<tr>
<td>KCl-control</td>
<td>KCl</td>
<td>110±57</td>
<td>0</td>
<td>–</td>
</tr>
<tr>
<td>KCl-20 nm</td>
<td>KCl</td>
<td>110±57</td>
<td>20±10</td>
<td>$3.14\times10^{-21}$</td>
</tr>
<tr>
<td>KCl-40 nm</td>
<td>KCl</td>
<td>110±57</td>
<td>40±10</td>
<td>$3.76\times10^{-21}$</td>
</tr>
<tr>
<td>KCl-75 nm</td>
<td>KCl</td>
<td>110±57</td>
<td>75±5</td>
<td>$4.10\times10^{-21}$</td>
</tr>
<tr>
<td>KCl-95 nm</td>
<td>KCl</td>
<td>110±57</td>
<td>95±5</td>
<td>$2.97\times10^{-21}$</td>
</tr>
</tbody>
</table>
4.1 Introduction

In the last decade, nanoparticles have been used in wide range of applications due to their unique optical, magnetic, thermal properties, and most importantly, easy manufacturability in large quantities [106–108]. One specific aspect of utilizing nanoparticles involves dispersing them in different solvents, polar or non-polar, for nanocatalysis [109], drug delivery [110], biotechnology [111], nanocomposite [112], and nanofluid applications [113–115]. To accomplish this, nanoparticles must be coated with an appropriate agent to produce compatibility with the solvent and
prevent phase separation and precipitation. In this paper, we present a one-step, highly controlled, all-dry method to tailor the wettability of the nanoparticles by depositing thin coatings of amorphous hydrogenated carbon in a glow discharge from a suitable precursor molecule. This nanoscale gas phase coating technique is independent of the nanoparticle structure, chemical reactivity and material type. The nanoparticles can be made hydrophobic or hydrophilic, depending on the precursor chosen during plasma treatment. Thus, this adaptable technique can be applied to a wide range of nanoparticles to produce compatibility with an equally wide range of fluids.

In general, good dispersion of nanoparticles occurs in solvents with functional groups similar to that of the coatings. Colloidal suspensions in the nanometer size regime have been intensively studied for polar solvents by dispersing common inorganic nanoparticles (e.g. silica, copper oxide, titanium oxide, etc.) [116]. The underlying critical challenge in developing these solutions is prevention of nanoparticle aggregation to ensure a long shelf-life. Typically, pH, temperature, and electrolyte concentration provide good control the stability of nanoparticle dispersion [117]. Hydrophilic particles cannot be dispersed in non-polar solvents without surface treatment. Grafting small molecules on the nanoparticle surface is a common approach to provide compatibility in non-polar media and prevent aggregation [118]. However, techniques that require chemical bonding impose restrictions on the types of molecules that can be grafted on a given substrate material such that methodologies are not adaptable from one system to another. The grafting process itself also can result in unwanted aggregation, especially if it requires processing at temperatures and pH outside the range for colloidal stability.

We have previously shown in Chapter 3 that deposition in glow discharges from
various organic precursor molecules can be successfully applied to very small (less than 100 nm) particles [56]. The solid film formed in plasma from hydrocarbon or fluorocarbon precursors is an amorphous hydrogenated or fluorinated carbon. Although these films lack the regular structure of common polymers, they do retain to a certain extent the chemical character of the precursor molecule, and this characteristic can be exploited to tune the hydrophobic/hydrophilic nature of the films.

4.2 Experiments

Three different precursors, isopropyl alcohol (IPA), toluene, and perfluorodecalin (PFD), were used as the reactant of the plasma deposition process for coating silica and copper oxide nanoparticles. Figure 4.1 depicts the experimental procedure for coating nanoparticles in the plasma enhanced chemical vapor deposition (PECVD) reactor. Dry powders of silica or copper oxide were first suspended in ethanol and was sonicated for 10 minutes. Then, ethanol was evaporated under the fume hood and the resulting sample was incubated in a desiccator. Particles are placed inside of the glass reactor tube with inner diameter of 1 inch and 1.24 inch outer diameter while for depositing a uniform radial coating, they have been agitated by a magnetic stirrer bar. One end of the reactor was connected to the vacuum system and its pressure was maintained around 200 mTorr during the deposition process. The other end was connected to a gas bubbler which was kept in a water bath with a constant temperature. The gas flow rate was maintained between 0.5 to 0.6 sccm by controlling the temperature of the water bath. Three different hydrocarbons that were used for these experiments were kept in the gas bubbler while
their water bath temperature was different. Water bath temperature was 35-37 °C for IPA, 43-45 °C for toluene, and 30-35 °C for PFD. Hydrocarbon gas and argon were mixed in the bubbler while the argon flow rate was 6 sccm for all the experiments. After reaching the constant pressure, 200 mTorr, a glow discharged was formed in the glass tube where particles were scattered on its surface between two electrode rings. The RF plasma was formed and sustained using an ENI ACG-3 XL RF power generator equipped with an ENI MW-5D automatic matching network. The plasma was sustained at 30 watts for IPA and at 40 Watts for toluene and PFD. This assembly provided a suitable reaction condition for coating of two grams of nanoparticles. Coated silica or copper oxide particles were removed from the reactor wall and were incubated in a desiccator before mixing them with different liquids. Depending on the volumetric fraction of samples, a measured amount of coated solid particles were mixed with liquid and was sonicated. We have used water and ethylene glycol as the polar solvents, dodecane as the non-polar, and

Figure 4.1: Schematic of the procedure for nanoparticle preparation, PECVD coating, and dispersion of nanoparticles in different solvents.
perfluorocyclohexane as the non-polar and lipophobic solvent. For dodecane fluid 20 mM sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was prepared and mixed with coated particles.

4.3 Results and Discussion

To observe the deposited thin film on the surface of coated particles, transmission electron microscope was used. Micrographs confirm that silica and copper oxide particles were coated uniformly in the plasma, as shown in Figure 4.2 and Figure 4.3. Transmission electron microscopy is a dry state characterization technique, therefore particles are transferred from a liquid suspension to the surface of the TEM sample holder. The TEM sample holder is a copper mesh covered with a very thin layer of carbon. Carbon is transparent but some liquids such as oil covers its surface and makes it blurry. Therefore, we have separated coated particles from oil by centrifuging the sample and dispersing particles in IPA for TEM grid preparation. Since coated particles with toluene and perfluorodecalin are hydrophobic, they aggregate on the surface of TEM sample holder as shown in Figure 4.2 and 4.3. Aggregation makes imaging of a single and separated particles challenging. Figure 4.2(a) and Figure 4.3(b) show silica and copper oxide particles coated with IPA plasma polymer respectively. As shown in Figure 4.2(b) and Figure 4.3(c) SiO$_2$ and CuO particles are nicely coated with toluene plasma polymer. Deposition of perfluorodecalin on the surface of silica and copper oxide was observed which is uniform all around SiO$_2$ and CuO particles as illustrated in Figure 4.2(c) and Figure 4.2(d). Thin film thickness is controlled by deposition duration and
Figure 4.2: Transmission electron micrographs of (a) silica particles coated with IPA, (b) silica particles coated with toluene, (c) silica particles coated with PFD plasma polymer.
as explained in Chapter 3, there is a linear relationship between time and film thickness, while the rate of deposition is around 1 nm/min.

Figure 4.3: Transmission electron micrographs of (a) uncoated copper oxide particles, (b) copper oxide particles coated with IPA, (c) copper oxide particles coated with toluene, and (d) copper oxide particles coated with PFD plasma polymer.

The hydrophobic properties of the plasma coating was evaluated by measuring the contact angle of water on silicon wafers that were spin-coated with plasma treated nanoparticles. For comparison, we deposited the same coatings on silicon wafers (in the absense of nanoparticles) and measured the water contact angle. An uncoated wafer was also used as a control. To compare the effect of coating on wettability properties of a surface, uncoated wafer and uncoated copper oxide spin-coated on the wafer were tested first; measured water contact angles were 60°
and 54° respectively. The coating produced by IPA increases the water contact angle as shown in Figure 4.4(b) and (f). Toluene plasma polymer coating is more hydrophobic and the contact angle exceeds 90° (Figure 4.4 (c) and (g)) for this coating. The highest contact angle was observed on coatings produced by PFD, which exhibits strong water-repellant properties, as shown Figure 4.4 (d) and (h). Substrate material plays no role in hydrophobicity of a surface which means just the coating is important. Graph (i) in Figure 4.4 illustrate this fact because the slope of each line is approximately the same. This means that the rate of increasing the water contact angle is the same for coated wafers or coated particles.

The dispersibility of plasma-treated particles was tested different solvents shown in Table 6.1. The degree of dispersion was quantified by measuring the hydrodynamic diameter of the suspended particles by dynamic light scattering and comparing to the size of the original Ludox silica (37 nm).

Table 4.1: Solvents Used for Preparing the Colloidal Suspensions

<table>
<thead>
<tr>
<th>plasma coated particles</th>
<th>solvents that particles can be dispersed in</th>
</tr>
</thead>
<tbody>
<tr>
<td>isopropyl alcohol</td>
<td>water, isopropyl alcohol, 1-butanol, ethylene glycol</td>
</tr>
<tr>
<td>toluene</td>
<td>hexane, toluene, dodecane, poly-alpha-olephin, jet oil</td>
</tr>
<tr>
<td>perfluorodecalin</td>
<td>perfluorocyclohexane</td>
</tr>
</tbody>
</table>

Amorphous silica showed good dispersibility in EG which is similar to the same electrostatic forces between particles that is present in aqueous silica solutions. Silanol groups on the surface of silica particles form hydrogen bond with ethylene glycol molecules and cause partial polarization in the solution [119]. Silica and copper oxide particles coated with IPA showed a better dispersion in water and ethylene glycol (EG) compared to uncoated nanoparticles. Depositing IPA plasma coating result in a thin film that has carbonyl group in its structure. The chemical
Figure 4.4: Left column shows the contact angle measurements on the surface of coated wafers with different plasma polymers and right column shows spin-coated wafers with coated copper oxide particles. Sessile water droplet contact angle measurements on the (a) uncoated, (b) IPA coated (c) toluene coated, (d) PFD coated, (e) copper oxide spine-coated, (f) IPA copper oxide spin-coated, (g) toluene copper oxide spin-coated, (h) PFD copper oxide spin-coated silicon wafer. (i) shows contact angle for different coatings on the surface of a silicon wafer or coated nanoparticles.
functional groups of coated particles with IPA plasma polymer are defined by using FTIR and are shown in Figure 4.5. The absorption peaks for IPA at 2930 cm\(^{-1}\) ascribe to C-H stretch and at 1710 cm\(^{-1}\) correspond to C=O stretch which could arise from aldehydes or ketones. Peaks at 1457 cm\(^{-1}\) and 1360 cm\(^{-1}\) shows C-H stretch, bending and rocking, in alkanes. Coated particles with IPA also showed better dispersion in water at normal pH and also in EG which is due to the effect of new functional groups on the surface. Zeta potential of the coated particles in water at neutral pH is -53 mV which is higher than uncoated silica particle zeta potential, -37 mV, at the same pH.

Particles coated with toluene cannot be dispersed in water but were well-dispersed in dodecane. For stabilizing hydrophobic particles in non-polar solvents we followed a typical protocol to control charging behavior and repulsive electrostatic
interactions of particles by introducing reverse micelles [120]. Plasma polymerized toluene coating results in stabilization of particles in non-polar media with long chain of carbon-hydrogen and hinder particles from being dispersed in polar and other non-polar solvents such as fluorocarbons that carbon-hydrogen is absent from their structure. Although perfluorous are very non-polar [121], they are not miscible with toluene and our experimental results show particles coated with toluene plasma polymer do not mix with perfluorocyclohexane. Using FTIR also supports that chemical structure of solid toluene plasma polymer is similar to the chemistry of organic compounds with hydrogen and carbon in its structure. Figure 4.5 depicts one of the main peaks for toluene which was observed at 2920 cm$^{-1}$, that according to literature shows the C-H bond. Other peaks were also detected at 1600 and 1470 cm$^{-1}$ that refers to the C=C stretching in ring and C-H scissoring respectively.

And finally utilizing plasma polymerized PFD for coating nanoparticles is the novelty of our method to suspend particles in fluorocarbon liquids. FTIR result shows a sharp peak at 1220 cm$^{-1}$ referring to carbon fluorine bonds on the surface of coated particles. We successfully mixed PFD coated particles with perfluorocyclohexane which arises from the similarity between the chemistry of the coating and the solvent. On the other hand, water contact angle measurements depict that plasma polymerized PFD is very water repellant [122]. Despite this fact that the hydrophobic particles should be dispersed in non-polar solvents, we found that PFD coated particles are not stable in non-polar solvents such as dodecane. Carbon fluorine bonds makes particles hydrophobic and lipophobic therefore PFD coated particles only form stable suspensions in perfluorocarbon liquids such as
perfluorocyclohexane.

4.4 Conclusions

In conclusion, by employing plasma polymerization, we successfully developed an all-dry method to coat nanoparticles in a dry-state to manipulate their wetting properties. Based on water contact angle measurements of coated wafers and spin-coated wafers with nanoparticles, we quantitatively measured the decrease in surface energy of nanoparticles. Controlled tuning the wetting properties of nanoparticles lead to formation of stable suspensions in polar, non-polar, and lipophobic solvents. Due to the great adhesion of solid thin-films deposited in plasma systems to any particle type with diameter ranging from nanometers to microns, this method may be useful in a variety of applications.
Chapter 5

Development of Hydrophobic Coatings for Oil- and Refrigerant-based Nanofluid by Plasma Deposition

5.1 Introduction

Cooling and heating fluids have been used in many industrial processing applications and promising theoretical and experiments results have been achieved that dispersion of nanoparticle in the fluids improves their thermal properties [17, 18, 123–125]. Colloidal suspensions that have been employed for heat transfer applications or so-called nanofluids are considered as an enhanced heat transfer fluid due to their higher thermal conductivity compared to the base fluid. Typical heat transfer liquids such as water, ethylene glycol and oils have significantly low
thermal conductivity, $\kappa$, compared to solid materials specially metals and metal oxides [126]. Therefore, adding particles specially to oils significantly improves thermal conductivity of the solvent. Existing experiments and theories demonstrate that addition of particles improves thermal properties however, clustering, aggregation, and pressure drop are some negative consequences of mixing particles with fluids [123, 127]. The best solution to overcome these drawbacks is choosing particles from nano-size scale to improve suspension stability.

Oils are one of the primary candidate for heat transfer liquid since they can reach high temperature (around 400°C) with no boiling or reaching the vapor phase [128] and also remain liquid in extreme low-temperature [129]. For example, poly-a-olefin (PAO) is a very common coolant that its initial boiling point is 410°C. On the other hand, refrigerants also have special thermodynamic properties such as high critical point and high heat of evaporation. But both oils and refrigerants that have suitable thermodynamic properties, suffer from having a very low thermal conductivity. For example PAO thermal conductivity is 0.15 which is very low compared to even water that has thermal conductivity of 0.81 and really low compared to solids such as copper oxide or alumina that have thermal conductivity of 20 and 35 respectively [18]. Some studies have been developed experimental methods to improve thermal conductivity of oils [130–132] and refrigerants [133–135] with nanoparticle suspension. The nanoparticles used in the oil-based nanofluid were carbon particles, carbon nanotubes, multi wall carbon nanotube [130,131,136,137], and TiO$_2$ [138]. As it is reported [130,131,136,137], carbon-based materials are the most suitable particles for oily environment. Suspending inorganic materials due to their hydrophilic properties causes aggregation, unless through some surface modification organic particles adapt hydrophobic or lipophilic properties [139]. Oils are
not the only fluids that have hydrophobic properties, refrigerants also have specific physical characteristics that makes the process of particle suspension difficult. Since 1995 due to state regulation it is illegal to use chlorofluorocarbons (CFCs) as refrigerants due to their ozone-depleting and high flammability. One of the best environment friendly alternatives are hydrofluorocarbons (HFC) [140]. Since only some works have been studied traditional refrigerants nanofluids [133–135], there is a great demand for suspending particles in new alternative fluids.

Plasma deposition has been developed to coat nanoparticles in dry-state with great adhesion to different solid materials [29,56,141–143]. Plasma process produces a solid amorphous hydrogenated carbon or so-called plasma polymer from different hydrocarbons and exhibit similar chemical and physical properties as the initial hydrocarbon. Since most of the hydrocarbons are immiscible with water, plasma polymers show strong hydrophobic properties [78,122,144]. In addition, plasma polymers fabricated from perfluorocarbons in plasma show hydrophobic and lipophobic properties which is compatible with hydrofluorocarbon environment [145,146]. In this work, we introduce a deposition process to tune nanoparticle surface for a stable suspension in oils and refrigerants. Toluene is employed as the plasma reaction precursor to modify hydrophobic properties of nanoparticle. Perfluoro-n-octane and perfluorodecalin are other reactants in plasma deposition for producing lipophobic and hydrophobic nanoparticles to produce refrigerant-based nanofluid. Then, we measure thermal conductivity of nanofluids by using transient hot wire (THW) method. Thermal conductivity of oil-based suspensions enhances up to 30% compared to the base fluid.
5.2 Experimental

5.2.1 Preparation of Dry Nanoparticles

Freeze-drying is a common method for preparation of dry particles by removing the solvent through a sublimation process at a very low temperature. Mixing freeze-dried particles with water and re-suspending them in water showed formation of many aggregates in water. It has been demonstrated that freeze-drying of even stable colloidal suspensions causes formation of agglomerates and in order to prevent the aggregation problem some pretreatment in the solution is needed. Lyoprotective agents (LPA) or lyoprotectants were mixed with particles in solution prior to the freeze-drying step. Silicon oxide powders were prepared using a Labconco freeze dryer. Colloidal suspension of silica particles was frozen by submersion in liquid nitrogen and frozen-dried at low pressure (10 mTorr provided by Edwards pump model RV3) and temperature of -50°C. After 12 hours, all the liquid was collected from particles, resulting dry powders. Since even small amount of water causes aggregation, particles were washed with alcohol and were dried under a fume hood after the freeze drying process. Copper oxide particles were prepared from a dry sample purchased from MKNano (division of M K Impex Corp.). Dry powders were suspended in ethanol and was sonicated for 10 minutes. Then, ethanol was evaporated under the fume hood and the resulting sample was incubated in a desiccator.

5.2.2 Particle Coating

The deposition process uses a radio frequency (RF) generator to create a low-pressure plasma in a tubular reactor as discussed in Chapter 2 and 3. Two alu-
minimum rings that serve as electrodes are located 1 inch apart from each other around the glass tube, where coating of particles occurs. The glass reactor consists of a tube with diameter of one inch that has a sealing flange at one end and is connected to a hydrocarbon flask and argon gas from the other end. Particles are transferred from the desiccator into the reactor by means of a spatula. In order to connect the reactor to the vacuum system, a metal clamp is used to seal one end of the reactor to the pipe that goes to the roughing pump. The glass reactor only has one inlet and one outlet. The inlet is connected to a glass flask which is sealed with a plastic o-ring and a nut to the inlet pipe. A constant flow of precursor and argon is delivered to the reactor during the entire process. The reactor pressure increases from 1 mTorr to 200 mTorr and stays constant for the entire deposition process. Argon flow rate is constant for all the experiments and is controlled at 6 sccm using a gas flow controller. Precursor gas flow also is also controlled at the constant rate of 1 sccm however for its controlling another process has been followed. In this work we have used four precursors, isopropyl alcohol (IPA), toluene, perfluoro-n-octane (PFO), and perfluorodecalin (PFD), while each precursor has different boiling point. In order to maintain the precursor flow rate around 1 sccm, the glass flask that contains the precursor is kept in a water bath with constant temperature. Water bath temperature was 35-37 °C for IPA, 43-45 °C for toluene, and 30-35 °C for perfluoro-n-octane and perfluorodecalin. Deposition process starts by connecting electrodes to the RF generator and operating the source of power at 30 W. During the entire process of deposition, particles are agitating by a magnetic stirrer which was placed inside of the reactor with particles. Stirrer shakes particles at speed of 100 rpm to provide a suitable condition for formation a uniform coating around particles.
5.2.3 Preparation of Nanofluids

Coated silica or copper oxide particles are removed from the reactor wall and are incubated in a desiccator before mixing with different liquids. Depending on the volumetric fraction of samples, a measured amount of coated solid particles is mixed with liquid and is sonicated. For dodecane and poly-a-olefin (PAO) fluids 20 mM solution of sodium Di(2-ethylhexyl) sulfoisuccinate (AOT) is prepared and is mixed with coated particles with toluene plasma polymer. Hsu et al. demonstrate affect of AOT on stabilization of hydrophobic particles in non-polar solvents [120]. The AOT forms reverse micelles in polar-solvents and changes the thermodynamic balance in the solution and improves particles interactions in order to stabilize the colloidal suspension.

5.3 Results and Discussions

In order to increase thermal conductivity of fluids, we have suspended two different nanoparticles, SiO$_2$ and CuO, in different solvents. In this regard, surface properties of particles have been tuned to be adaptive to the solvent by depositing a plasma polymer thin-film. Silica particles before coating have average diameter of 37±3 nm and Figure 5.1 (a) shows field emission scanning electron micrographs of silica particles after they were treated in plasma for 10 minutes. As depicted in Figure 5.1 (a), SiO$_2$ particles preserve their spherical shape after the deposition process. Copper oxide nanopowders before coating do not have a controlled shape and size while have a size distribution as shown in Figure 5.2. Although the average size is 100 nm, the size variance is large. Particle irregular shape is observed in FESEM and this shape is preserved after coating as shown in Figure 5.1 (b).
We have investigated the preparation and plasma deposition on silica nanoparticles and have found that IPA, toluene and PFD plasma polymer successfully form uniform coating around particles. Copper oxide particles also have been coated with IPA, toluene, PFO, and PFD and Figure 5.3 depicts transmission electron micrographs of coated CuO with toluene and PFD. Thin-film has uniformly surrounded each particles with thickness of 50 nm. Both TEM and FESEM provides information about morphology, thin-film thickness and particle size however since both techniques are dry-state characterization techniques, we cannot measure the average size of each sample using these methods. Dynamic light scattering has been used after suspending particles in different solvents to measure particle size while they are in the solution. Before measuring size, we have to find the best solvent for each coated sample based on the coating characteristics to have stable suspensions. Particles coated with each precursor preserve chemical characteristic of the hydrocarbon that they were deposited from. One of the most important characteristics of plasma polymers directly inherited from the parent precursors is their hydrophobic properties. In order to study the impact of different coating on
water-repellency and hydrophobicity of particles, copper oxide nanoparticles were coated with different precursors in plasma. We have prepared 5 different samples of particles: uncoated copper oxide, copper oxide coated with isopropyl alcohol, toluene, perfluoro-n-octane, and perfluorodecalin plasma polymer. In order to observe their behavior when they come in contact with water, we have mixed 50 mg of particles in a vial with 10 ml of water and have shaken each sample for one minute. After 1 hour while they were left on the lab counter, we have observed them. Uncoated copper oxide particles were mixed with water as shown in Figure 5.4 (a) as well as coated particles with IPA, Figure 5.4 (b). But particles coated with toluene and perfluoro-n-octane floated on top of the water surface, Figure 5.4 (c) and (d). Coated particles with perfluorodecalin not only did not tend to mix
with water and floated on water surface but also were attracted to the surface of the glass escaping from the water surface. Coated particles behavior can be explained by understanding the chemical characteristics of each precursor. Isopropyl alcohol (IPA) is a polar solvent and is miscible with water. Plasma polymer deposited from IPA is also miscible with water having hydrophilic properties. Toluene is a saturated hydrocarbon which is not miscible with water, therefore coated particles with toluene show hydrophobic properties. On the other hand perfluoro-n-octane and perfluorodecalin are also immiscible with water and are not only hydrophobic but also they show lipophobic properties as shown in Figure 5.4 coated particles with PFO and PFD are really hydrophobic.

To fabricate nanofluids, coated silica and copper oxide particles were dispersed in different solvents after plasma deposition process. We have coated silica and copper oxide particles with IPA, toluene, PFO, and PFD and have suspended them in water, ethylene glycol, 1-butanol, hexanes, dodecane, perfluorohexanes,
Figure 5.4: Miscibility of coated copper oxide particles with water. (a) uncoated copper oxide, (b) coated copper oxide with IPA, (c) coated copper oxide with toluene, (d) coated copper oxide with perfluoro-n-octane, (e) coated copper oxide with perfluorodecalin mixed with water.

and poly-a-olefin (PAO). After mixing coated dry particles with each solvent, they were sonicated for 40 minutes and their size was measured using dynamic light scattering (DLS) and the size was monitored for 14 days. In Figure 5.5 we describe the average size of silica particles, Figure 5.5 (a), and copper oxide particles, Figure 5.5 (b), dispersed in different solvents. Re-dispersion of uncoated silica particles without controlling pH was not possible, particles aggregate and show average size of 530 nm at pH of 6.7. Perceptible dispersion of coated particles with IPA plasma polymer in water, 1-butanol, and ethylene glycol (EG) was observed. Dispersing them in water without controlling pH show a better dispersion compared to uncoated silica since particles average diameter is 474±27 nm, which is less than the average size of uncoated particles, 530 nm, at the same pH. Ethylene glycol is a better candidate for dispersing uncoated and coated silica with IPA compared to water. According to the result shown in Figure 5.5, coated silica nanopar-
particles with IPA have smaller diameter, approximately 170 nm, compared to the uncoated silica particles, 270 nm. Electrostatic interactions described by the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) explains the repulsive forces. Repulsive interactions cause formation of a stable suspension with less aggregates. Therefore, particles coated with IPA have more ability to repel each other which means more charge reside on their surfaces. Zeta potential measurements are done to provide information about the particle surface charge. Zeta potential of the coated particles in water at neutral pH is -53 mV which is higher than uncoated silica particle’s zeta potential, -37 mV, at the same pH because IPA plasma polymer coating has carbonyl group in its structure. Higher surface charge on coated nanoparticles leads to more stable suspension in polar solvents such as water and EG.

![Graph showing size of silica and copper oxide nanoparticles in different solvents with different coatings.](image)

**Figure 5.5:** Size of (a) silica and (b) copper oxide nanoparticles measured in different solvents coated with different materials.

Coated particles with toluene plasma polymer are more hydrophobic than IPA coated silica particles therefore it was impossible to mix them with water and
ethylene glycol. As shown in Figure 5.4 (c) particles stays on top of water while uncoated silica and coated silica with IPA are mixable with water. Toluene was mixed with hexanes and dodecane. The average size for each sample show that hydrophobic particle are dispersed better in non-polar solvents as shown in Figure 5.5. Coated particles with perfluorodecalin are really hydrophobic and we observed that particles just float on the surface of water and even by mixing, shaking and sonicating prevent them from being soaked in water (Figure 5.4 (e)). We mixed superhydrophobic coated silica nanoparticles with dodecane and observed that after 10 minutes and 20 minutes of sonication average size of the particle is 700 and 360 nm respectively. We continued sonication and after 50 minutes a well dispersed sample was produced and the average diameter measured by DLS was 110 nm as shown in Figure 5.6 (a). This sample is not stable and over time its average diameter increases as illustrated in Figure 5.6 (b) while after one day particles average size becomes 1200 nm which means most of the particles have aggregated and have formed big agglomerates. Changing the solvent and using perfluorohexane as the base fluid results in a well dispersed and a very stable colloidal suspension. As shown in Figure 5.5 average diameter of particles is around 80 nm which shows a well dispersion of particles in perfluorohexane solvent. Similar study has been done for copper oxide and their behavior is exactly the same as silica nanoparticles as depicted in Figure 5.5 (b). In respect of the result showing particle size in different solvent, we are able to suspend any particle in both oil- and refrigerant-based fluids. New refrigerants, hydroflurocarbons, nanofluids can be fabricated by suspending coated particles with PFO or PFD and oil-based nanofluids can be formed by suspending coated particles with toluene.
Figure 5.6: Coated silica with perfluorodecalin dispersed in dodecane. (a) Size of the particles for different sonication time and (b) size of the particles after 50 minutes of sonication.

Thermal conductivity of different nanofluids for heat transfer applications have been measured and thermal conductivity ($\kappa$) enhancement of three different suspensions is illustrated in Figure 5.7. Transient hot wire tests [147, 148] have been employed to measure the effective thermal conductivity of nanoparticle suspensions. Transient hot wire (THW) test cell is consist of a 14 cm platinum wire with plastic end cap that is vertically supported by a glass test cell that hold the test fluids. This wire that is connected to the source of power serves as the heat source while simultaneously its temperature is measured which interpret the electric resistance of the wire. Thermal conductivity of the nanofluids is estimated by using Fourier’s law of conduction based on the measured temperature during the hot-wire test. Eapen et al. [18] recently have studied thermal conductivity ($\kappa$) enhancement models and have proposed that the classical Maxwell theory is able to predict thermal conductivity improvement of nanofluids within two boundaries. The lower bound can explain a geometry configuration where nanoparticles are
dispersed in the solvent and solvent is the continuous phase and the upper bound can explain the opposite configuration. They have analyzed a large body of experimental data and have found that the results lie between the lower and upper Maxwell bounds. In Figure 5.7, upper bound and lower bound are represented by a solid line and a dashed line respectively. Figure 5.7 (a) shows thermal conductivity enhancement of suspended silica nanoparticles coated with IPA plasma polymer in EG. Thermal conductivity of ethylene glycol (0.26 W/m-K) compared to water is low, about one half of that of water, but since its boiling point is almost two times larger than water boiling point, it has been used as industrial heat transfer fluid. Adding silica to EG improves their thermal conductivity, $\kappa$. Suspending particles with higher thermal conductivity such as copper oxide ($\kappa = 20$) remarkably changes the thermal conductivity of the fluid as shown in Figure 5.7 (b). Oils have very low thermal conductivity and adding particles may improve their $\kappa$ significantly. Even preparing 1 vol% copper oxide changes the thermal conductivity of dodecane up to 40% as shown in Figure 5.7 (c).

Figure 5.8 shows the thermal conductivity of nanofluids, CuO suspended in poly alpha olefin (PAO), with different concentration as a function of time. Thermal conductivity of each sample decreases with elapsed time and the rate of thermal conductivity reduction is higher for more concentrated samples. For the very dilute sample with 0.1 vol% concentration no decrease has been observed but increasing the volumetric concentration to 0.5, 0.7, and 1 vol% causes a noticeable decrease in thermal conductivity of the nanofluids. According to the Stokes law, settling velocity is:

$$ V = \frac{2.R^2}{9.\mu}.(\rho_p - \rho_l).g $$  \hspace{1cm} (5.1)
Figure 5.7: The experimental result represented by dot symbol for conductivity of (a) coated silica particles with IPA in ethylene glycol (b) coated copper oxide particles with IPA in ethylene glycol, and (c) coated copper oxide particles with toluene in dodecane. The solid and dashed line denote the Maxwell classical bounds for thermal conductivity of nanofluids.
Where it depends on the radius of particles, $R$, density of particle, $\rho_p$, density of the base liquid, $\rho_l$, and viscosity of the base liquid, $\mu$. Most of the metals and metal oxide particles have a high density compared to the base fluid, almost 6-8 times larger than the liquid density, therefore according to the Stokes law particles settle down faster. Another parameter that affects the velocity is the liquid viscosity which is not really high for most of the oils. But the most effective parameter is particles radius. For example, CuO particles with radius less than 100 nm settle down in a container with height of 14 cm in a month. But here for measuring the thermal conductivity, first we put samples in the thermal conductivity meter with height of 14 cm. Particles start to settle down fast for this system and in one hour half of the particles settle down. After one experiment we have sonicated samples for 20 minutes and have repeated the experiment again. We have obtained the same result for the second time which demonstrate that particles are not chem-
ically aggregated, just due to a low stability because of their high density, they settle during time. According to particle size distribution, Figure 5.2, and FESEM images of particles, Figure 5.1, some particles with large diameter (500nm-1000nm) exist in the solution. Precipitation of these large particles is around 30 minutes in PAO and that is the main reason that we observe reduction in nanofluid thermal conductivity.

5.4 Conclusions

We employ plasma enhanced chemical vapor deposition (PECVD) to improve surface properties of nanoparticles. We adapt the hydrophobic characteristics of plasma polymer coating on nanoparticle surfaces, which produces a surface with hydrophilic, hydrophobic, or super-hydrophobic properties. These particles are then used in polar, non-polar, oil, and refrigerant fluids to form nanofluids. We find hydrophilic particles treated in isopropyl alcohol (IPA) plasma show more stability in polar solvents due to their higher surface charge. and hydrophobic coating deposited from toluene stabilize particles in oils such as dodecane and PAO. We also demonstrate superhydrophobic particles prepared in perfluorodecalin plasma can form a unstable dispersion in oils since they have lipophobic properties. Therefore, we suspend them in hydrofluorocarbons that are considered as new type of refrigerants. We also measure thermal conductivity of nanofluids and demonstrate that it depends on sample concentration and can be improved up to 30% for samples with volumetric concentration of 1. However, for higher concentration of copper oxide particles due to presence of particles with diameter larger than 500 nm particles precipitate faster. Thus, in order to introduce more stable solvents we can employ
smaller particles.
6.1 Introduction

A high performance energetic material (e.g. explosives, rocket fuel) should store large amounts of chemical energy and, on demand, be able to release it instantly. Metal particles are considered as prime additive candidates in energetic materials application as they are readily oxidizable and release large amounts of heat during the oxidation process [149, 150]. In particular, aluminum particles are currently being considered in advanced energetic materials application such as solid rocket boosters fuel [151]. The major drawback of using aluminum particles is their low rates of energy release compared to other carbon-based energetic compounds (e.g. TNT, HMX, and RDX) [152]. This is a critical limitation due to some oxidation kinetics. Some strategies have been followed to improve the kinetics of the oxidation reaction. One strategy is using fine nano-sized particles with diameter less than 100 nm instead of larger particles. Another strategy is adding an oxidizer
agent to nanoparticles to improve the heat of release during the oxidation reaction. The reason to follow the first strategy is that the combustion of micron-size aluminum particles does not perform complete combustion but nanoparticles with diameter less than 100 nm have shown to exhibit complete combustion [153]. The primary challenge of using nanoparticles is the formation of oxide layer on their surfaces [154, 155]. A passivation aluminum oxide layer forms when particles are exposed to air and humidity. And the contribution from this oxide layer to the total weight content may reach to a high value compared to the initial body weight of a fine nanoparticle. Coating nanoparticles with a protecting passivating layer needs to be developed especially before formation of the oxide layer to prevent oxidation and contamination of aluminum nanoparticle [156–158]. Herein, we discuss a process to passivate aluminum nanoparticles with a thin-film produced through a low-pressure plasma enhanced chemical vapor deposition process (PECVD). Low pressure system provides a good reaction condition where particles are not exposed to air and humidity. This coating also works as an oxidizer at high temperatures which enhances the combustion energy through which more aluminum oxide forms and higher energy releases from the combustion process.

The most common passivation technique involves formation of oxide shell [159]. However, formation of oxide layer reduces the active metal content of nano-seized particles and adds resistance to the combustion kinetics. In addition to this problem, the formed oxide layer is permeable to oxygen and water molecules and the oxidation process would persist during long storage conditions. Surface coating of aluminum with other noble metals or metal oxide is another approach to modify the surface of aluminum nanoparticles and prevent oxidation [152]. For example Foley et al. followed a reduction/deposition process by adding soluble salts of sil-
ver, gold, and nickel. They showed that these metals increased active aluminum content of nanoparticles and also enhanced energy content of combustion while inter-metallic reactions happen to metallic coatings. Boron in another attractive material for stabilization of aluminum nanoparticles propellants [160,161], because boron-coated particles can increase the powder combustion enthalpy [160,162]. On the contrary, boron-coated particles react with water having a very short induction period. Park et al. coated nanoparticles with carbon utilizing a DC arc or laser ablation method to passivate particles [163]. Considerable amount of work has been performed by Jouet et. al. on surface passivation of aluminum nanoparticles using perfluoroalkyl carboxylic acids (C_{13}F_{27}COOH) based on wet chemistry method [19,164]. The C_{13}F_{27}COOH coating can be performed directly on the oxide shell or on oxide-free aluminum particles. However, unless the nanoparticles are prepared in situ [165], the wet chemistry method would not prevent the growth of oxide shell formation. To overcome some of the above-mentioned problems, a suitable coating technique is needed for nano-sized aluminum that can be applied for large-scale production of passivated aluminum nanoparticles. The coating should form an impermeable shell to water and oxygen in ambient temperature, but enhances the rate of Al oxidation at elevated temperatures and possibly participates in the oxidation process.

A convenient method for large-scale production of passivated aluminum would involve synthesis of impermeable shell to water and oxygen in ambient temperature and a coating that increases the rate of Al oxidation at elevated temperatures. An oxidizer is typically added to aluminum mixture in propellants [166–168]. Oxidizers diffuse to the particle surface at elevated temperatures when particles are melting and then also diffuse through the aluminum oxide that forms on particles
surface while the particles are burning [169]. Decreasing particles size improves oxidation [149, 170, 171] of aluminum in the combustion process and addition of oxidizer provides a suitable condition to have a complete combustion [172]. Among different chemicals and elements fluorine is the most powerful [173], oxygen is the second most powerful and nitrogen, chlorine, boron, and carbon are the other strong oxidizers. Koch [174] has evaluated the combustion of fluorocarbon/metal in energetic materials and have found that fluorocarbons have a great potential as oxidizers in propellents. Perfluorinated aluminum particles show improvement in the kinetics of aluminum oxidation compared to the untreated particles [175]. Among the fluorocarbons that he has investigated, those that has both C-F and C-C bonds are powerful oxidizers [174]. Some other studies [176] also show that using fluorine as an oxidizing agent in propellents produce more heat during the combustion and adding fluorine oxidizer to micrometer-scale aluminum particle improves the combustion to achieve the same performance that we can obtain by using nano-scale particles.

A unique technique that produces hydrophobic coating consist of fluor and carbon materials is plasma enhanced chemical vapor deposition [51,177,178]. Plasma deposition utilizes excited molecules, ions, and radicals of hydrocarbon monomer molecules in gas-phase and deposit a solid amorphous hydrogenated carbon or so-called plasma polymer. Plasma polymer thin-film have been tailored for protection of flat metal substrates [179–181]. In the present work, plasma polymerization coating technology has been utilized to coat aluminum nanoparticles. We focus on two important benefits of using highly cross-linked amorphous hydrogenated carbon deposited on aluminum surfaces. The first advantage of a carbon-based coating is that they are hydrophobic hence the thin-film blocks diffusion of air humidity
and protects aluminum nanoparticles against oxidation. The second advantage is that they increase enthalpy of combustion by participating as an oxidizer in the combustion reaction.

6.2 Experiment

6.2.1 Materials and Preparations

Aluminum nanoparticles (99.9+%) were purchased from Nanostructured and Amorphous Materials Inc. Nanoparticles were incubated in a desiccator under inert atmosphere after they were transferred from their original container into small vials in a glovebox of argon to prevent oxidation and contamination. During the entire process they were not exposed to air or humidity since the experiment was done in a vacuum system. Different hydrocarbons with variety of functional groups were used as the precursor of the plasma deposition. Isopropyl alcohol (IPA 99.5%) and perfluorodecalin (PFD 99%) were obtained from VWR while toluene was purchased from EMD chemicals.

6.2.2 Plasma Coating of Aluminum Nanoparticles

The set-up for plasma polymerization process is shown in Figure 6.1. This apparatus is constructed from four different systems: hydrocarbon delivery system, tubular reactor, vacuum pumps and pressure controllers, and radio frequency generator equipped with a matching box. Prior to the deposition process, 10 ml of each organic precursors was measured and was poured into a glass flask connected to the reactor via a vacuum pipe. The temperature of this flask is maintained con-
stant at 35°C for isopropyl alcohol and perfluorodecalin and at 45°C for toluene. The glass flask is a bubbler for vapor delivery with one inlet, which is connected to an argon gas cylinder equipped with a gas flow controller. Argon flow rate is constant (6 sccm) and mixes with organic vapor in the bubbler with flow rate of 1 sccm. The mixture of argon and vapor enters the reactor at constant flow rate during the deposition process. Exactly before connecting the reactor to the pump, aluminum nanoparticles are transferred to the reactor. We use a metallic spatula for transferring particles from the glass vial into the tubular reactor. A small magnetic stirrer is also left inside of the glass tube for the purpose of particle mixing. The tubular glass tube is connected to the pump through a vacuum pipe which is sealed to the tube using an o-ring and a clamp. After tightening the clamp, we gradually open the check valve between the pump and the reactor. As soon as the reactor pressure reaches 200 mTorr, we turn the radio frequency power on while the matching box is working. Two external electrodes separated one inch from each other are designed where the one that goes around the glass tube is connected to a 13.56 MHz radio frequency power source. The plasma is maintained at 30 W when IPA or PFD are the precursor of the plasma deposition and at 40 W when we are using toluene. Plasma deposition takes place between two electrodes where we spread the particles. In order to shake particles and have a uniform radial thickness of coating all around particles, the glass tube was placed on top of a magnetic stirrer working at 100 rpm. A liquid nitrogen trap with cool wall is employed in the system and designated in the system to condensate organic vapors before entering the pump. When deposition process is completed, we close the gate valve and bring the reactor back to atmospheric pressure. Particles are collected from the reactor wall ad were incubated in the desiccator.
6.2.3 Characterization of Coated Nanoparticles

To ensure particles are individually coated and measure the thickness of the coating, transmission electron microscopy (TEM) was done using a Philips (FEI) EM420T. To investigate morphology and observe conspicuous change on the surface of Al nanoparticles when they were exposed to air, field emission scanning electron microscopy (Leo 1530 FESEM) was used. The crystal and phase structure was done using X-ray diffraction (Panalytical Xpert PRO MPD theta-theta diffractometer) using Cu radiation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed on a TA Instruments SDT 2960 that does simultaneous DSC-TGA under an air flow of 40 mL/min. To obtain micrographs of aluminum wafers, scanning electron microscopy (SEM Hitachi S-3500N) equipped with a diffraction energy microscopy (EDS) was used.

6.3 Results and Discussions

To protect and passivate aluminum nanoparticles three different coatings were deposited on the surface of nanoparticles in the plasma reactor. Micrographs
collected using TEM confirm formation of a plasma polymerized thin film around the nanoparticles. Thin-film deposited through plasma enhanced chemical vapor deposition of isopropyl alcohol is adhesive to different materials [56] and here we show the result of coated aluminum nanoparticles in Figure 6.2(a) with IPA plasma deposited solid thin-film. Plasma polymerized isopropyl alcohol was deposited on Al nanoparticles with average thickness of 30 nm. To control the thickness, we control the deposition time knowing that the deposition rate is approximately 1 nm/min [56]. Figure 6.2(a) depicts Al particles coated with IPA plasma polymer for 30 minutes and measuring the coating confirms formation of 30±5 nm thin film around particles. This technique has a great potential to deposit thin films of few nanometers, and here we show Al nanoparticles that were coated with toluene and PFD plasma polymer for 7 and 10 minutes respectively (Figure 6.2 (b) and (c)). The plasma polymer layer deposited from toluene and PFD also show a great adhesion to the surface of particles when plasma parameters such as argon and precursor flow rate are tuned to obtain the pressure of 200 mTorr during the deposition process.

The unique characteristics of plasma polymerized coating produced from toluene and PFD is their water-repellent properties. Figure 6.3 demonstrates sessile water droplet contact angle with a coated silicon wafer with different plasma polymers that we have used for coating aluminum nanoparticles. Plasma polymerized IPA has more hydrophilic properties since water contact angle with this coating is 84±2. As it was discussed in our earlier report [56], this barrier is permeable to water and small solute molecules such as KCl and silica. But toluene and PFD plasma polymers are more hydrophobic and coated particles with these materials do not mix with water. Contact angle of a water droplet with toluene plasma polymer is
higher than 90°, 92±2, and for PFD plasma polymer is 125°. By simply mixing IPA plasma polymer coated KCl particles with water, the KCl trapped in the hydrophobic coating may dissolve in water and gradually and release from the shell. Conductivity meter is used to quantify the amount of KCl that was dissolved in water as a function of time. The profile release of coated KCl with toluene and IPA plasma polymer is shown in Figure 6.4. We predicted a slow release of ma-
terial from core which is because of the slow diffusion of water into the shell, dissolution of KCl in water inside the shell, and diffusion of dissolved KCl through the shell. This process is illustrated by Figure 6.4 for IPA coated KCL but is not valid for toluene coated KCl. To investigate the difference between coatings, we have considered their major difference which is the wettabitlity of the thin films. Figure 6.3 reveals that toluene coating is hydrophobic which means water could not diffuse into the shell. In this regard we observe no dissolution of KCl even after 5 days. We only observed a fast release at the beginning of the dissolution process which is due to some half coated or not coated KCl particles.

Figure 6.3: Water contact angle measurements of coated silicon wafer with isopropyl alcohol (IPA), toluene, and perfluorodecalin (PFD).

Hydrophobic thin films produced in plasma from toluene and perfluorodecalin are very protective coatings because they are impermeable to water. Most of the corrosive reactions like reacting with sodium hydroxide takes place in aqueous so-
Figure 6.4: Profile release of coated KCl with toluene, and IPA in water. IPA coating is not hydrophobic and is permeable to water, so the solid line shows its controlled release over time. Toluene coating is hydrophobic, therefore the profile release just show small amount of KCl that was dissolve just after mixing KCl particles with water. None of the core material was dissolve as shown by dashed line.

solution. Repelling water automatically protect aluminum substrate against sodium hydroxide. A solution of 0.5 molar NaOH was prepared and two different aluminum wafer were covered with this solution. Before pouring NaOH solution on Al wafer, scanning electron microscopy (SEM) was used to capture some images from its surface. Aluminum wafer surface as shown in Figure 6.5(a) is a smooth surface with some waves and marks that were formed during the polishing process. A similar wafer was covered with NaOH solution and was washed with DI water after 5 hours. Micrographs taken from the aluminum surface, Figure 6.5 (b), show a ruined aluminum wafer with a rough surface. On the other hand, Figure 6.5 (c)
depicts coated aluminum wafer with PFD plasma polymer that was covered with NaOH solution for 5 hours and no significant change (Figure 6.5(c)) compared to the uncoated one (Figure 6.5(a)) was detected.

Figure 6.5: SEM images of (a) uncoated aluminum wafer, (b) uncoated aluminum wafer exposed to NaOH, (c) and coated aluminum which is exposed to NaOH.

To compare protective properties of each coating, 4 different samples were
tested while they were in the same environment. Samples of uncoated aluminum, coated Al with IPA, toluene, and PFD were kept in a closed container at 85% relative humidity and 25°C. After two months, samples were collected and first were tested using FESEM. Aluminum particle surfaces are very smooth and rounded as depicted in Figure 6.6 (a), however they could not conserve their spherical shape when they are exposed to air and harsh humidity. Oxidation affects the surface morphology and roughens smooth surfaces of the particles. Oxidation effect is shown in Figure 6.6 (b) which reveals a rough surfaces, damaged, and corroded particles. On the other hand, the surface appearance of coated particles with PFD were as smooth and as rounded as the uncoated particles that were not exposed to air and humidity. Further observation using TEM in Figure 6.7 revealed that aluminum nanoparticles have reacted with oxygen and not only a layer of oxide was formed on particles but also due to the harsh environment and humidity some roughens on the surface is observed. Although the passivated layer of oxide prevent core of the aluminum powder from further reaction, almost only 20% reactive aluminum remains after exposure to air and humidity. But coated particles with PFD plasma polymer stay intact while all of the aluminum content is preserved (Figure 6.7 (c)). Energy dispersive spectroscopy supports oxide formation on bare particles after exposure to air and humidity. Chemical composition of the uncoated particles that were kept in the glovebox, that were exposed to air and humidity, and coated with PFD plasma polymer is shown in Figure 6.8. Since particles were placed on a silicon wafer, in each spectrum a strong peak of silicon was observed. The spectrum shown in Figure 6.8 (a) present a strong peak which corresponds to aluminum while no oxygen was detected. Oxygen was detected in aluminum sample that was exposed to air(Figure 6.7 (b)) however no oxygen was detected in
the coated one (Figure 6.8 (c)).

Figure 6.6: Field emission scanning electron micrographs of aluminum particles that were (a) transferred from glove box to a sealed container, (b) exposed to air and humidity, and (c) coated with perfluorodecalin and were exposed to humidity and air.

To determine aluminum content of different samples, thermogravimetric analysis is performed in air. Since combustion enthalpy of Al depends on the size of particles, they were chosen from a narrow range of size, 80-100 nm. By gradually heating up the aluminum nanoparticles, the metal reacts and forms alumina. From the weight gained during the heating process, the amount of active materials can be determined. Other possible gain weight due to oxinitride and aluminum nitride formation [182] may take place if self-ignition happens [183]. Gaining weight rapidly and receiving heat by a fast rate cause self-ignition, while preventing that is possible by heating with a slow rate. The rate of heat to the system was controlled and the sample was heated with a fast rate of 20 °C/min at the beginning of the experiment until the temperature reached 350 °C. Then we heated the sample at slower rate of 5 °C/min from 350 °C to 600 °C followed by a faster heating rate, 20 °C/min, from 600 °C to 850 °C. Before cooling down the system we waited for 4 hours to ensure that all of the aluminum has reacted.

The thermogravimetry profiles for 5 different samples are illustrated in Figure 6.9. The first change in weight loss profile for all different samples is observed below
Figure 6.7: Transmission electron micrographs of aluminum particles that were (a) transferred from glove box to a sealed container, (b) exposed to air and humidity, and (c) coated with perfluorodecalin and were exposed to humidity and air.
Figure 6.8: Energy dispersive spectroscopy (EDS) graphs of Al nanoparticles (a) uncoated kept in glovebox, (b) uncoated exposed to air and humidity, and (c) coated with PFD plasma polymer exposed to air and humidity.

350°C which is due to the evaporation of water and other volatile vapors. Aluminum particles that were kept in glove box were not exposed to air and humidity; TG profile supports this fact since only 3% of weight loss occurs at temperatures lower that 350°C. The initial weight loss for other samples is more that that and is different based on their surface hydrophobicity. The least hydrophobic particles are uncoated aluminum powders which absorbed 20% water and other vapors, black solid-line in Figure 6.9, and this amount decreases by increasing the degree of hydrophobicity. Isopropyl alcohol, toluene, and perfluorodecalin plasma polymer lose 8, 4.2, and 4% of their weight respectively while IPA plasma polymer is the least hydrophobic coating, toluene plasma polymer is hydrophobic and PFD coating is very hydrophobic. Presence of water has two effects on the active content of aluminum. The first one is that the oxide film thickness increases in humid air compared to the dry air therefore the active aluminum content decreases [184]. And the second effect is that the reaction of water with active aluminum results in formation of hydrogen, aluminum hydroxide or oxide depending on the tem-
perature of the reaction [156]. Therefore, water can react with aluminum and reduce the active content of nanoparticles. The second change in sample weight by increasing temperature in TG profile happens between 350°C to 500°C which is due to the oxidation of aluminum. Around 500°C, all the samples stop gaining weight for almost 20 minutes where oxide layer reaches a thickness that stops further oxidation. But around 700°C where each samples produce enough energy to melt the oxide barrier, oxidation process continues and each sample start to gain more weight. All remaining aluminum reacts until the weight level off and reaches its maximum amount. As shown in Figure 6.9, the aluminum powder that was exposed to air and humidity gained only 20% weight due to the oxidation. However, the weight gains for more hydrophobic particles that were kept in the same condition are higher than the uncoated sample. Coated Al with IPA gained 52% weight and coated Al with toluene and PFD gained 58% and 60% weight respectively due to oxidation which means that they have more active aluminum content than the uncoated sample kept in the same environment. Even comparing coated aluminum with each other shows more hydrophobic samples gained more weight which reflects that coatings preserved most of the active materials.

A distinguishable difference in thermogravimetric analysis (TGA) result between uncoated aluminum that was kept in a glovebox with no humidity and coated particles was observed, Figure 6.9. Around 700°C a dramatic weight gain for all coated samples and uncoated aluminum was detected. But at the end of the process, uncoated particles gained less weight compared to coated samples. Possible explanations for a better oxidation is that the amorphous hydrogenated carbon and fluorocarbon polymer thin films have permeable shell where oxygen have a better diffusion. And also the combustion enthalpy of carbon based mate-
Differential scanning calorimeter (DSC) was conducted for uncoated aluminum kept in a glovebox, uncoated Al that was exposed to air and humidity and three different coated samples with IPA, toluene, and PFD that were exposed to air and humidity. Differential Scanning Calorimetry (DSC) measures the heat flows and temperature associated with transitions in aluminum nanoparticles as a function of temperature.
Figure 6.10: DSC graphs of uncoated Al stored in a glovebox and coated Al with different coatings placed in the air after a month with RH of 90%.

of time and temperature as shown in Figure 6.10. Each profile provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity. The plasma deposited coating on particles start to degrade at temperature around 250°C and the exothermic process due to cross-linking of carbon-carbon and carbon-fluorine which occurs around this temperature is shown in figure 6.10, the first peak. The main peak due to the exothermic decomposition occurs around 520°C for uncoated aluminum sample, 541°C, 542°C, and 555°C for toluene coated, IPA coated, and PFD coated Al respectively. Heat of combustion is determined for each sample by measuring the area of the DSC peak on a time basis. Coated samples show a significant increase for the heat of combustion compared to the uncoated aluminum. Table 6.1 compares enthalpy of combustion for all different aluminum samples. Since aluminum content of uncoated sample that was exposed to air is the lowest, its combustion enthalpy is also the smallest amount, 2.15 k/Jg. Aluminum nanoparticles that were protected from oxidation by storage in a glovebox
show a higher enthalpy of combustion (3.12 kJ/g). The most interesting result from DSC measurement is the high enthalpy observed for combustion of coated samples. Coatings protect aluminum nanoparticles and at high temperature, above 500°C, improve oxidation process. Both TGA and DSC confirm the ability of coatings to protect active component of aluminum nanoparticles and increase the heat of combustion. Levitas et al. [185] showed with differential scanning calorimetry (DSC) that aluminum nanoparticles with diameter of 17 nm that were not mechanically damaged have 2.627 kJ/g heat of combustion. Compared to their result, coated aluminum even with 100 nm diameter release more energy during the oxidation process. Another interesting comparison is with the result that Gue e. al [186] have shown. They have coated Al nanoparticles with hydroxyl-terminated polybutadiene and have stored particles for 2 years. Differential scanning calorimetry results show that coated particles have high enthalpy change (3.87 kJ/g) compared to uncoated particles. The deposited coating plays a great role in order to protect the aluminum content. Comparing their DSC result with DSC profile of the Al that were kept in a glovebox shows that they have protected particles from oxidation. Comparing the DSC results of our coated samples with their coated aluminum sample reveals that plasma deposited thin-films has a higher impact on improvement of the change of enthalpy.

Table 6.1: Enthalpy of Combustion for Coated and Uncoated Aluminum Particles

<table>
<thead>
<tr>
<th>Samples</th>
<th>Enthalpy of combustion ((\Delta H) [kJ/g])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum kept in the glovebox</td>
<td>3.12</td>
</tr>
<tr>
<td>Uncoated aluminum exposed to air and humidity</td>
<td>2.15</td>
</tr>
<tr>
<td>Coated aluminum with IPA and exposed to air and humidity</td>
<td>4.2</td>
</tr>
<tr>
<td>Coated aluminum with toluene and exposed to air and humidity</td>
<td>4.40</td>
</tr>
<tr>
<td>Coated aluminum with PFD and exposed to air and humidity</td>
<td>4.65</td>
</tr>
</tbody>
</table>
6.4 Conclusions

We developed a process to passivate aluminum nanoparticle surfaces via a dry state process. Low-pressure plasma enhanced chemical vapor deposition of isopropyl alcohol (IPA), toluene, and perfluorodecalin (PFD) was conducted on the surface of Al particles with average diameter of 100 nm. Deposited thin-films showed hydrophobic properties which help preventing water adsorption and increasing the possibility of oxide formation on the surface of particles. Prepared transmission electron micrographs of coated and uncoated particles confirm that hydrophobic coatings protect particles from oxidation even in a very harsh environment with RH of 85%. Scanning electron micrographs were prepared from coated aluminum exposed to NaOH and proved that this coating provides enough resistivity against corrosion and chemical reaction on the surface of aluminum. Coatings protect all of the active content of Al nanoparticles and improves their burning behaviors at elevated temperatures. Thermogravimetric analysis and differential scanning calorimetry determine the Al content and heat of combustion for each sample. Coated samples show also an improvement compared to the aluminum nanoparticles that were protected inside of a glovebox. In fact, the coatings also work as an oxidizer and melt the formed oxide layer at high temperature and help the oxygen permeate better to burn the entire content of each aluminum nanoparticle.
Chapter 7

Microbubble Formation from Plasma Polymers

The majority of the work presented in this chapter was previously published in the Journal of Physical Chemistry B [187].

7.1 Introduction

Hollow micro/nanospheres are materials that provide a means for storage, insulation, and for fabrication of low density devices and foams. [188–190] They are potentially useful as encapsulation vehicles for drugs, cosmetics, gene, DNA, enzyme, [191–194] as catalytically active materials and as acoustical and thermal insulators. [195–197] Because of their distinctive scattering and adsorption properties, they have been used in pigment and paper coating applications. [198,199] Hollow nanoparticles are prepared either through a template-assisted or through a template-free method. In the template-assisted process, a core particle (template) is coated with the shell material and the template is then removed chemically or
by thermal decomposition [200]. The template-assisted method has been used for large-scale fabrication and for synthesis of hollow particles with different sizes and shapes. In the template-free method the hollow particle is produced in a single step through various mechanisms, including flame pyrolysis of liquid droplets [201, 202], liquid-to-solid conversion, [93, 203–205] and crystal dissolution equilibria [206]. The template-free method is more challenging because it is not easily generalized from one material to another, but it presents the significant advantage that it does not require the additional processing steps involved in template-assisted processing.

Several inorganic materials have been made into hollow spheres in a one-step process involving an inside-out evacuation procedure, which has been explained by a dissolution-recrystallization mechanism that was first described by Wilhelm Ostwald [206, 207]. Hollow structures can also be formed by exposure of particles to temperature, pressure, and pH shifts, and by absorption of energy in the form of electric and magnetic fields, light [208–211], and in some cases under the irradiation of electron beam when the sample is studied in TEM. [212, 213] These examples highlight the variety of mechanisms by which homogeneous particles may be transformed into core-shell nanostructures.

Conventional polymeric materials have been observed to produce hollow nanoparticles by the one-step process [214]. Plasma polymers (PP) are non-conventional solids that can form nanoparticles as well as hollow nanospheres [56, 93, 215]. Over the past 60 years plasma polymerization has been used to coat substrates with thin films [5, 42, 216] for applications in biological, pharmaceutical, and electrical systems [142, 217–219]. Plasma polymerization mostly occurs in low-pressure electrical discharges when organic gases and vapors, such as methane, isopropanol, parylene, toluene, and etc., are delivered to the plasma [220, 221]. The gas dis-
charge produces reactive species from the original gas or vapor monomer and the final product is typically a solid material that consists of a cross linked network of amorphous hydrogenated carbon. These materials are chemically inert and exhibit low friction and low dielectric constant. [222, 223] Though mainly plasma polymers are deposited as films, it is also possible to produce nanoparticles via gas phase nucleation [53, 224, 225]. Particles by plasma polymerization have been used for plastic and rubber products, nanofluids, and controlled release applications because of the controllability over their size, hydrophobic properties, and their mechanical properties [226, 227]. The degree of cross linking depends on the operating parameters of the plasma but generally, high power and low pressure promote the formation of solid materials with a high degree of cross linking whereas low power and higher pressure promotes the formation of viscous oily liquids [228, 229]. In this work, we describe the formation of liquid-like nanoparticles in a toluene plasma that undergo a liquid-to-solid transformation to produce solid microbubbles, namely, micron-size spheres that consists of a thin solid shell and a large empty void in the middle. We present material characterizations of the microbubbles, investigate energy sources that can induce the solidification of the bubbles, and present evidence for the proposed mechanism of formation.

### 7.2 Experimental

#### 7.2.1 Synthesis

Particles were produced in a semi-batch tubular pyrex reactor as shown in Figure 7.1 by plasma polymerization of toluene in a pressure less than 400 mTorr. Toluene (99.5 % pure) was obtained from J. T. Baker as the feed supply for the
reaction. The reactor chamber consists of two parts that are connected with a flange sealed by a metal clamp ring. This connection point provides a port to access to the pyrex reactor for the purpose of collecting particles. Toluene vapor and argon gas enter from the top via a 0.25 in diameter pipe. The plasma is generated by two aluminum rings placed outside the glass reactor at a distance of 3 cm from each other. The top ring is connected to the radio frequency (RF) power supply and the bottom one is grounded. The RF power supply is connected to an automatic matching network and produces an RF signal at 13.56 MHz whose power is manually controlled from 5W to 20W. The toluene vapor was delivered to the reactor using a glass bubbler that was connected to the flow of carrier gas (argon). Toluene vapor flow rate was 2 sccm while the argon flow rate was 12 sccm. The temperature of the bubbler was kept constant in a water bath in order to deliver toluene with specific flow rate and minimum excess. Argon flow rate was controlled using a mass flow controller while toluene vapor flow rate was controlled by the water bath temperature. Particles formed by the decomposition of toluene in the plasma and were collected on the surface of a filter placed at flange that links the two parts of the reactor. The vacuum is produced by a roughing pump equipped with a liquid nitrogen trap. The reactor pressure before delivering argon gas and toluene vapor was 1 mTorr and was increased to a higher pressure of 200 mTorr or 400 mTorr, during the experiment. Excess vapor was condensed on the cold surface of the liquid nitrogen trap to prevent pump from contamination.
Figure 7.1: Schematic representation of the vertical glass reactor used for plasma process to produce nanoparticles with the picture of the reactor.

### 7.2.2 Characterizations

Transmission electron microscopy (TEM) studies were conducted in a Philips 420 instrument. Particles were collected on 200 square mesh copper grids. Videos and transmission electron micrographs were recorded and captured using a digital CCD camera connected to TEM. Scanning electron micrographs were acquired on a Leo 1530 field emission scanning electron microscope (FESEM) to study morphological
characteristics of the particles. Fourier transform infrared (FTIR) spectra were obtained in the range from 850 cm$^{-1}$ to 4000 cm$^{-1}$ using Bruker IFS 66/S FT-IR spectrometer.

7.3 Results

Particles collected from the plasma appear in TEM as dark spheres (Figure 7.2(a)), approximately 1 μm in diameter. Almost immediately upon focusing the beam, these particles begin to grow and expand until a stable micron-sized bubble is formed, with solid walls and a large void, as seen in Figure 7.2(b). The final particle is a solid bubble, about twice as large as the original particle, with thin walls that appear solid and remain stable under further irradiation by the electron beam. The conversion process has been observed multiple times in real time and was captured by video. (See the video in the Supporting Information.) A series of images extracted from the video (see Figure 7.3) show the entire process. The first panel (Figure 7.3(a)) shows the particle 0.6 s after focusing the beam. This particle appears as a dark compact sphere with the highest contrast (darkest point) at the center. At about 1 s, Figure 7.3(b), a small void forms at the center of the particle and is recognized by the lighter contrast at the middle. Within the next 10 s the diameter grows rapidly, the interior of the particle becomes lighter, and the location of the highest contrast moves from the center to the circumference. Within 12 s of focusing the beam, the particle is fully transformed into a micron-sized bubble with thin solid walls. A small contraction of size is generally observed right before the bubble reaches its final size (see panels i and j in Figure 7.3). Figure 7.4 shows the size of the same particle, plotted as a function of time. The
size increases roughly linearly with time and exhibits a small contraction before it settles to its final value. This behavior was observed with all particles on the grid, and was reproduced between independent runs of the reactor. Observation under tilted angles show that the microbubbles are nearly perfect spheres (Figure 7.5b and c) except at the contact point, Figure 7.5d. This image also shows that the small circle that appears to be form in the middle of the bubble (see panels c
Figure 7.3: Transmission electron micrographs of a single 3.23 µm toluene plasma polymer at (a) 0.6, (b) 1.05, (c) 1.84, (d) 2.24, (e) 3.62, (f) 4.6, (g) 5.48, (h) 6.33, (i) 7.5, and (j) 12.4 seconds after exposure to the 120 KeV electron beam, the scale bars are 1 µm.

Through j in Figure 7.3 is the contact area between the bubble and the substrate. Hollow spheres have a radially uniform shell thicknesses of 47±18 nm and a high void fraction that is 90±3% of the volume of the particle. The size distribution before and after exposure to TEM is shown in Figure 7.6. The average diameter approximately doubles after exposure to the TEM beam, from an initial size of 0.83±0.26 to 1.60±0.60 microns. These numbers are averages from three hundred and twenty independent experiments. We note here that heptane under the same conditions was also observed to produce microbubbles. For the remainder of this study, however, we will focus on toluene exclusively.

Particles before and after exposure to TEM were collected, pressed into a KBr pellet and studied by Fourier Transform IR spectroscopy (FTIR). The spectrum of particles before exposure to TEM (Figure 7.7a) shows a strong adsorption peak at 3050 cm\(^{-1}\), which is characteristic of the aromatic CH stretches, typically present in the 3050-3090 cm\(^{-1}\) range [230]. Absorption bands are observed at 2980 cm\(^{-1}\) and
1660 cm\(^{-1}\), corresponding to sp\(^3\) C-H (alkyl) stretching and alkene group, C=C, respectively. After exposure to the beam (Figure 7.7b), the spectrum contains adsorption bands at 2860 and 2930 cm\(^{-1}\) that are assigned to alkyl CH stretches. The most important difference is in the aromatic group, which is clearly present before exposure to electron beam but absent after irradiation. Accordingly, particles formed in the plasma retain a significant degree of the chemical structure of the precursor molecules (toluene), but this is subsequently lost when particles are exposed to the TEM beam. This shows that the beam induces further reaction that completes the transformation of the precursor into the final solid material.

The formation of microbubbles occurs under the action of the electron beam in
Figure 7.5: TEM pictures of a single hollow particle with different tilting angles, (a) 0, (b) 10, and (c) 30 degrees. (d) Side view of a hollow microbubble.

the TEM but other forms of energy induce the same transformation. Specifically we examined the effects of laser irradiation and heating. For the laser experiments, particles were subjected to a pulsed laser beam irradiated from an argon laser (Coherent Innova 300C) for one minute with two different intensities, 3423.5 W/cm², and 6847 W/cm² while they were suspended in an aqueous solution. Figure 7.8 shows TEM images of the particles after treatment. The images show the presence of large hollow particles. Though these particles do not have the smooth
Figure 7.6: Size distribution for particles before and after exposure to electron beam.

appearance of those formed under TEM, they are clearly of the same type, and consist of a thin shell that surrounds a large empty core. No formation of new bubblew is observed when these particles are examined in TEM, indicating that the transformation was complete under laser irradiation.

Heating provides yet another means of converting the plasma particles into hollow spheres and offers additional control of the process via temperature. For this experiment, four samples of particles collected from the plasma were subjected to heating in a furnace (thermolyne model FB1400) at constant temperature (100, 200, 250 and 300 °C) for 5 minutes. Their TEM images in Figure 7.9 indicate that hollow particles begin to form at a temperature as low as 100 °C. Particles heated to 200°C and 250°C show a collapse of structure into a rough, spherical particle with significant porosity. At 300°C they are completely collapsed, leaving behind a porous solid residue.
Figure 7.7: Transmission electron micrographs and FTIR of plasma polymerized toluene particles: (a) before exposure to e-beam, (b) after exposure to e-beam, and (c) formed at RF power of 20 W.
7.4 Discussion

The decomposition of hydrocarbon molecules in the plasma is often described as a polymerization process. Although the product is not a true polymer with a repeating monomeric unit, it is a solid of cross-linked amorphous hydrogenated carbon [2]. Typically the final material is solid, but liquid-like products, sometimes referred to as oils, are also known to form under conditions that promote low degree of cross-linking. Generally, low pressure and high power promote the formation of solid products, whereas low power and high pressure produce materials with a low degree of cross-linking that appear as oily films [228, 229, 231] or, as our results suggest, as micron-size droplets. In the experiments shown here, the plasma is operated at 400 mTorr and RF power of 5 W. Under these conditions we expect the formation of oily materials. To confirm this hypothesis we repeated the experiments at 200 mTorr and 20 W of RF power. Figure 7.7c shows parti-
Figure 7.9: Affect of temperature on toluene plasma polymerized particles. Transmission electron micrographs of the particles at (a) at 100 °C, (b) 200 °C, (c) 250 °C, and (d) 300 °C.

...cles collected after 5 min of operation of the plasma. They are very small (less than 100 nm in diameter), have a solid appearance, and remain unchanged under TEM. Their FTIR spectrum shows the same bands at 2860 and 2930 cm$^{-1}$ as the solid bubbles that are formed after exposing the plasma particles to TEM. This confirms the presence of alkyl CH stretch (Figure 7.7c) and the absence of the
Table 7.1: Carbon-Hydrogen Ratios of Plasma Polymerized Toluene

<table>
<thead>
<tr>
<th>Sample</th>
<th>H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene PP (Oily) Before Exposure to e-Beam</td>
<td>1.01</td>
</tr>
<tr>
<td>Toluene PP After Exposure to e-Beam</td>
<td>0.95</td>
</tr>
<tr>
<td>Toluene PP (Solid)</td>
<td>0.95</td>
</tr>
</tbody>
</table>

aromatic group.

The elemental analysis of the plasma particles is given in Table 7.1. Three samples were analyzed: oily particles produced at low power (before exposure to TEM), microbubbles produced by exposing oily particles to TEM, and solid particles obtained at high power. The hydrogen-carbon ratio in all samples is less than in toluene (1.14). The solid particles and the microbubbles have very similar ratios, whereas oily particles before exposure to the beam have approximately 5% more hydrogen. In view of these results, the formation of microbubbles can be explained by the following scheme in which, liquid-like droplets with low degree of cross linking are converted into a solid material with higher degree of cross linking while releasing hydrogen:

\[
\text{oily droplets + energy} \rightarrow \text{solid bubbles + } \text{H}_2
\]

The bond dissociation energy of carbon bonds in plasma polymerized toluene is less than 7 eV (e.g. bond dissociation energy of C-C, C=C, and C-H is 3.61, 6.35, and 4.30 eV respectively [2]). Given that the incident energy of the electron beam is 120 KeV [232], and that the kinetic energy transferred to solids by the irradiation of the TEM beam is approximately 30 keV [57], breaking carbon bonding is indeed feasible. It appears, therefore, that the formation of microbubbles is due to the further polymerization of partially cross-linked oily droplets with the simultaneous
release of hydrogen, which explains the inflation of the bubble in TEM.

Electron beam irradiation in TEM has been reported previously to induce structural transformations in inorganic systems such as gold and platinum [233], to produce metal nanostructures from Ag, Ni, Cr, Al, and Au [234]. In these processes electron serves as the external driving force by losing portion of its kinetic energy due to inelastic interaction with materials. Besides TEM, high resolution scanning electron microscopy (HRSEM) [57] has been also used for producing nanorods and nanoparticles [57]. In one particular study, it was shown that gold structure changes due to exposure to the electron beam in TEM and dynamically changes the shape of the crystal and causes it grow [235]. Amorphous iron oxide, Fe$_2$O$_3$, nanoparticles were shown to evolve to larger particles while they were exposed to electron beam and formed hollow structure [212]. Similar evolution was observed for NaYF$_4$:Yb,Er nanoparticles in TEM because of the interaction with electron beam [213]. Although hollow polymeric particles have not been fabricated using electron beam, this method has been applied to induce cross-linking for modification of polymers (e.g. polyphenylene) in order to improve their shape, wear, and mechanical properties [236–239].

Formation of hollow nanoparticles by plasma polymerization was reported previously from a variety of organic precursors [93]. That process was also explained as a liquid-to-solid conversion but the hollow nanoparticles were formed inside the plasma, not under subsequent treatment, and the void fraction was much smaller, less than 4%. The unusual feature of the present process is the inflation of spherical particles into microbubbles with a large volume fraction of about 90%. Given the proposed scheme for the formation of these structures, we may write an expression
to relate the size of the initial liquid droplet to that of the final bubble:

\[
\frac{4\pi R_1^3}{3} \rho_1 = (4\pi R_2^2 h) \rho_2 + \delta m
\]  

(7.1)

where \( R_1 \) is the radius of the oily droplet, \( \rho_1 \) is its density, \( R_2 \) is the radius of the final bubble, \( h \) is the thickness of the shell, \( \rho_2 \) is the density of the cross-linked solid, and \( \delta m \) is the mass of hydrogen that is produced during cross linking. From 7.1 we estimate the mass of released hydrogen to be 0.5% of the mass of the liquid particle. The relationship between \( R_1 \) and \( R_2 \) then becomes

\[
R_1 = \left( \frac{3h\rho_2}{0.995\rho_1} \right)^{1/3} R_2^{2/3},
\]  

(7.2)

which implies a straight line between \( R_1 \) and \( R_2^{2/3} \). This relationship is plotted in Figure 7.10 based on the experimental data. Indeed, the data show a linear relationship with zero intercept, as predicted from Equation 7.2, with a slope of 0.603 nm\(^{1/3}\). The thickness of the shell is 47 nm and the density of the liquid particles is not known but we may approximate it with the density of liquid toluene, 0.86 g/cm\(^3\). Using these values, we use the slope of the line in Figure 7.10 to estimate the density of the solid particle, which we find to be \( \rho_2 = 1.25 \) g/cm\(^3\). Reported values for the density of plasma polymers are in the range of 1 to 1.5 g/cm\(^3\) [240, 241]. The value calculated from the experimental data falls in the middle of this range and this agreement lends further support to the mechanism of liquid-to-solid conversion that was used to interpret the formation of these bubbles.
Figure 7.10: Experimental data for different particles with initial radius of \( R_1 \) and final radius of \( R_2 \) are shown with open circles and the solid line shows the fitted line, which is in good agreement with Equation 7.2.

### 7.5 Conclusions

We have demonstrated a one-step process for formation of hollow particles from plasma polymerized particles. In this process, the plasma produces a partially polymerized liquid whose subsequent polymerization leads to the formation of a solid, the release of hydrogen, and the transformation of the liquid droplet into a microbubble with thin solid walls and high void fraction. This transformation was documented in detail using toluene as the precursor and was also observed with
heptane. The formation of liquid droplets by plasma polymerization is reproducible provided that the plasma is operated under low power and high pressure. The transformation of these liquids into microbubbles is induced by various forms of energy, including electron beam, laser irradiation, and heating. This suggests that oily microdroplets by plasma polymerization may be engineered to serve as stimuli-responsive materials.
Conclusions and Recommendations for Future Work

8.1 Conclusions

There is a growing interest in the use of nanoparticles for different applications. Physical, chemical, optical, and magnetic properties of particles can be tuned and modified by coating them with other materials. There has always been a great demand for developing new coating technologies. The main goal of this dissertation was also introducing a new process for coating nano-scale materials and developing facile procedure to control and change their properties. We have developed a process to control plasma enhanced chemical vapor deposition (PECVD) of different hydrocarbons on the surface of particles with diameter between 30 nm to 1 micron. Plasma deposited coatings have been employed in this project due to their major characteristics:

- Good adhesion to any material
• Permeable to small molecules

• Controlled hydrophobic properties

• Corrosion-resistance properties

The significant conclusions from this dissertation by utilizing plasma coating are summarized below.

Deposition of plasma polymer in the low-pressure reactor is discussed in Chapter 3 which can be adapted to the surface of nanoparticles with diameter less than 200 nm. Since solid thin-films formed in the plasma are adhesive to any material, I successfully coated silica nanoparticles and KCl nanocrystal particles. This process is capable of depositing a thin layer, as thin as 1 nm, up to thick coating of 100 nm. Deposition rate is 1 nm/min and thin-film thickness can be controlled easily by controlling the duration of deposition. After coating particle, they were suspended in a proper solvents to dissolve the core materials. By dissolving silica in hydrofluoric acid and KCl in water, we showed that the coating is permeable to small solutes (e.g., K⁺, Cl⁻) and water. However, plasma coating reduces the rate of core dissolution in a controlled way. Employing KCl as core materials provided an easy process to detect the concentration of dissolved ions of K⁺ and Cl⁻ using a conductivity meter. Monitoring the concentration while the core was dissolving shows the profile release of core. A model based on Fick’s second law was used to explain the experimental data. The model that predicts the rate of core release has a great agreement with experimental data. Based on the model, diffusion coefficient of the coating is very low, $3 \times 10^{-21}$ m²/s, which provides a great barrier for a slow controlled release. This slow release can even be extended over a long duration, for example one month, by controlling the thickness of the coating.
The results in Chapter 4 demonstrate the capability of the plasma deposition to control the hydrophobicity of particles. Utilizing three different hydrocarbons (isopropyl alcohol, toluene, and perfluorodecalin) as plasma precursors results in formation of hydrophobic coatings with different water repellent ability. Based on water contact angle measurements of coated wafers and spin-coated wafers with nanoparticles, we quantitatively measured the increase in hydrophobic properties of nanoparticles. Controlled tuning the wetting properties of nanoparticles lead to formation of stable suspensions in polar, non-polar, and lipophobic solvents. Studying the chemical structures of each coating shows that particles can be suspended in solvents that has the same functional groups as their surfaces. Stable suspensions of coated particles shows promising results as heat exchanger fluids (nanofluids).

In Chapter 5, thermal conductivity of stable suspensions of coated particles in typical solvents was measured which shows and improvement up to 40% for samples with 1% volumetric concentrations. In this chapter we demonstrate a suitable process for producing oil- and refrigerants-based nanofluids.

The experimental results in Chapter 6 show that the hydrophobic properties of plasma coating can be employed to protect aluminum nanoparticles against oxidation and contamination. Aluminum nanoparticles are the prime candidate as an additive to propellents and fuels due to the high energy that they release during the combustion process. Thin-film deposited on aluminum nanoparticles works as a barrier that limits adsorption of water and stops oxidation on the surface of particles. By protecting aluminum particles, the spontaneous oxide layer that forms after exposure to air and humidity, does not form. Therefore, the active aluminum content stays intact. Transmission electron micrographs prepared from
the surface of coated particles qualitatively show that no oxide is formed on the surface of coated nanoparticles. Quantitatively, we measure the active content of coated and uncoated aluminum particles using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results show that coatings inhibit oxidation during storage, where PFD coatings show the highest degree of protection and IPA the lowest. Although the films are porous and permeable by small molecules such as water, increasing the hydrophobicity of the coating improves substantially resistance against oxidation in the presence of moisture.

Chapter 7 focuses on the ability of plasma process to form nanoparticles. Plasma deposition reaction conditions such as reaction pressure, precursor flow rate, and power of the plasma control formation of particles or so-called "dusty plasmas". Since plasma technology focuses on the surface coating and tries to avoid conditions in which formation of particles takes place, defining particle formation region is very important. In Chapter 7, we show formation of particles is possible from toluene precursor by controlling power and pressure of the reaction. Not only nanoparticles form in plasma from toluene, but also applying low power of radio frequency generator provides a condition for formation of hollow particles. Responsive liquid-like particles with low cross-linking in their structures form in plasma which can be excited by different sources of energy (e.g., e-beam, heat, and laser) to produce solid micro-bubble. The hydrogen component of particles before and after exposure to the source of energy was measured and the result reveals that the hydrogen content of particles decreases after the exposure process. Release of hydrogen in the form of gas causes particle evolution like a bubble. The process of liquid-to-solid conversion can be explained using a simple mass balance equation. Using liquid-to-solid conversion can also predict the growth profile of bubbles and
estimate the density of solid bubbles which is around 1 to 1.5 g/cm³.

Overall, the results from this dissertation open new possibility to utilize modified nanoparticles in different applications ranging from drug delivery to nanofluids and metalized energetics. A new plasma system that is introduced in this work provides a great capacity to coat 1-2 grams of nanoparticles. Design of a new semi-flow reactor in vertical configuration also provides a novel set-up for producing particles in plasma. The novelty of this designed process is its ability to synthesize responsive particles to external stimuli.

8.2 Recommendations for Future Work

Additional insights into both studying the fundamental of the plasma deposition and tailoring coated particles in new applications can be accomplished in future studies. A succinct recommendation is provided in the following section for future investigations.

8.2.1 Experimental Set-up

The experimental set-up in the horizontal configuration which was discussed in Chapter 2 was designed for research purposes. Therefore, it is limited to coating of less than 2 grams of nanoparticles. However, since plasma conditions only dominate the quality of coating, a new reactor with larger diameter, 3-5 inch, can be design to coat larger quantities of nanoparticles. Another important improvement is designing an agitator inside the reactor to shake the particles constantly. Improving the shaking and stirring of particles, enhances the radial uniformity of the coating around particles for thick coatings.
8.2.2 Encapsulation Strategies

Although isopropyl alcohol is a promising candidate for material encapsulation and drug delivery purposes, it has not been tested in vivo. Plasma polymers with oxygen in their structure are biocompatible therefore there is a large promising opportunity for plasma polymers to be considered as drug carriers. For example, some studies have been done using plasma coating on biodevices [242,243]. Plasma deposited thin-films have been utilized in many different biomedical applications for manufacturing biodevices such as intraocular lens, hip and knee prostheses, heart valve, breast implant, and etc. Based on Kitching et al. study on plasma polymer coatings, they are biocompatible [243]. Many studies have been done using a wide range of hydrocarbon precursors for biomedical application [244]. The next step for this project is adapting biocompatible coating on the surface of particles for controlled release of drugs. Long-term release has been done by utilizing few polymers as drug carrier [13,100], therefore there is a great field of study in plasma polymer field to find coatings with really high degree of cross-linking to encapsulate materials for a long period of time.

Some studies on biodevices show that their hydrophobic properties should be improved when they are in contact with blood [245,246]. A great advantage of plasma deposition is its facile control over hydrophilic and hydrophobic properties of surface by choosing a proper precursor. According to the results discussed in Chapter 4 and 5, a method has been established to enhance particle hydrophobic properties by utilizing immiscible hydrocarbons with water such as toluene and perfluorocarbons in the plasma treatment. Hydrophobic coatings have a great applications for drug delivery since they can pass through the lipids and deliver drug only when they reach that region. Encapsulated hydrophilic drug in hydrophobic
materials will not mix with aqueous part of the body and can only target the lipid part.

8.2.3 Protective Thin-film on Wafers

All the experiments reported in this dissertation were conducted on the surface of nanoparticles. Although plasma technology is a well-developed technique for coating wafers, all the coating characteristics have not been studied for improving surfaces properties. For example, one novel result from this dissertation is that the hydrophobic coatings on Al nanoparticles protect them from oxidation and contamination. Metal wafers such as aluminum and silicon usually are protected against oxidation by a thin layer of the metal oxide that forms spontaneously on their surfaces when they are in contact with oxygen. However, this oxide layer cannot chemically protect them against other chemical reactions. Preliminary results in Chapter 6 demonstrates that hydrophobic coating can protect aluminum surface against a corrosive base such as NaOH. Quantitative studies can measure metal’s corrosion resistivity using electrochemical impedance spectroscopy (EIS). This method involves a reaction on the surface of aluminum wafers that works as electrodes in an electrical circuit. Based on the output impedance of the circuit, the reaction taking place on the wafer is determined. So for example if the impedance is stationary, no reaction has occurred and the wafer is not corroded. Some results are prepared during my collaboration with Advanced Cooling Technology in Lancaster, Pennsylvania. More experiments are required to find thick hydrophobic coating that protects aluminum against any reaction.

Plasma deposition also opens up possibilities for fabrication of anti-icing hydrophobic surfaces that have a great application for traffic lights. During winter,
traffic light glasses are covered with frozen water. To defrost and heat the glass surfaces, traffic light bulbs should be used instead of cheap and long life LEDs that can be used in warm and hot regions. Preliminary results show that moist and water falls down on the surface of vertical glasses coated with toluene and perfluorodecalin. Therefore, even in -5°C no ice was formed on the surface of the glasses. Future studies should be designed to demonstrate the feasibility to deposit transparent and superhydrophobic coating in plasma reactors.

8.2.4 Formation of Particles in Plasma and Their Application in Nanofluids

Radio frequency (RF) plasmas are widely used to synthesize carbon structures [224, 247, 248]. The main goal is producing large amounts with narrow size distribution which is possible by using plasma enhanced chemical vapor deposition working at high power of RF generators. Perfluoro-n-octane, toluene, heptane, and propylene were used as plasma precursors and fabrication of particles was observed only for heptane and toluene at power higher than 50 W with high flow rates of precursor. Additional study is needed in order to fabricate particles from more hydrocarbons to propose a logical explanation between particle formation and structure of the hydrocarbon precursor. Currently, plasma parameters are the known factors that control the deposition process. However, for some chemicals synthesis of particles is not possible. Therefore, more experiments with hydrocarbon from different organic groups such as alcohols and saturated hydrocarbons must be performed.
8.2.5 Formation of Microbubbles

Toluene precursor was the only hydrocarbon that was discussed in Chapter 6 for fabrication of responsive micro-bubbles. Formation of liquid-like material provides opportunities for fabrication of sensitive material in plasma. Some other chemicals such as poly(N-isopropylacrylamide) [242] are considered as thermally responsive coatings, which may also produce particles that are sensitive to external stimuli. Further experiments should be performed on more hydrocarbon that may show similar behavior as the bubbles demonstrated in Chapter 7.
Appendix A

Particle Preparation

A.1 Silica Particles

To prevent aggregation, dry samples also need some preparations. Very small nanoparticles can be purchased or synthesized in the lab in wet environment in the form of colloidal suspensions. Since plasma deposition is a dry-state reaction, special process for drying the sample is required.

A.1.1 Dry Silica

Large agglomerates form in dry state due to the environmental humidity. Water in the air works as a binder that holds particles together. Dry silica purchased from Gel tech incorporation, or fumed silica obtained from MkNano are mixed with ethanol and were sonicated for 10 minutes. Then, the particles were left under the fume hood in the lab until all the water and ethanol evaporates. To prevent further aggregation and humidity absorption, particles were incubated in a desiccator.
A.1.2 Colloidal Silica

Stable suspension of silica particles (LudoxTM-50 colloidal silica) was purchased from Sigma-Aldrich. Freeze drying was performed in material research lab facilities using 1 liter bench top freeze dryer (Labconco). One important suggestion is adding lyoprotectants to the stable suspension prior to the process [249]. Colloidal suspension should be placed in a plastic dish before putting it in the vacuum chamber of the freeze dryer. The sample needs to be frozen therefore the plastic dish is kept in a liquid nitrogen dewar before placing it in the chamber. Tailoring this technique provides a suitable process to produce smooth and non-aggregated samples.

A.2 Sodium Chloride and Potassium Chloride

Atomizer (Model 3076) is the system used for synthesis of salt particles discussed in Chapter 3. Atomizer produces aerosols and evaporates the solvent from the droplet of the aerosol which leads into the formation of small particles as shown in Figure A.1. Depending on the concentration of the sample, produced particle size is different. When the original solution concentration is low, the produced droplets in the atomizer carry small amount of the solvent. Therefore, after the evaporation process very small particles form. Particles discussed in chapter 3 were produced from a solution with 0.01 vol% of potassium chloride. Liu and Lee [250] have discussed the detailed information regarding the salt concentration and particle size in their manuscript. After collecting particles from the atomizer in a filter, they are incubated in a desiccator for 4 hours and were sift through a series of mesh before transferring them to the reactor.
A.3 Aluminum

Aluminum nanoparticles are really sensitive to air and humidity. Immediately after exposure to air, a thin layer of oxide forms with the thickness of 2-3 nm. For the special goals of chapter 5, particles were not exposed to air before, during, and after the coating process. Argon glovebox in department of chemical engineering is the first environment where particles were transferred from the sealed container received from Nanostructured and Amorphous Materials Inc. to a glass cuvette. The glass cuvette was also incubated in a desiccator prior the experiments. Since plasma reaction also takes place in a vacuum system there is no need to keep the reactor inside of a glove box.

A.4 Copper Oxide

Copper (II) oxide, CuO, was purchased from MkNano and was washed following the same procedure explained in section A.1. Particles average diameter is 100 nm.
Smaller particles with average diameter of 40 nm were purchased from American Equipment incorporation.
The actual system that we are working with is shown in Figure B.1. In order to model this system diffusion of water in the plasma polymer, diffusion of water in KCl, diffusion of dissolved KCl from core to shell, and diffusion of KCl in shell should be considered. This complicated modeling without knowing the diffusion coefficient of the material in plasma polymer is not possible. Using a simple equation to determine diffusion coefficient is possible for latter time during the dissolution process when core materials are dissolve in water in the entire shell as

![Figure B.1: Schematic of the core-shell.](image-url)
The mechanism of dissolution process is explained by Fick’s law. The distribution of the drug in the system for spherical coordinate, Figure B.2, is:

\[
\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{dr^2} + \frac{2D}{r} \frac{\partial c}{\partial r} \tag{B.1}
\]

where \( C_A \) is core concentration, \( r \) is the radius of the core and shell, and \( D \) is the diffusion coefficient.

For solving this equation we assume core materials are uniformly spread in the hollow particle and shell and there is a perfect sink condition. Sink condition means that the core concentration always reach a constant concentration on the particle surface. The initial and boundary conditions for solving this equation based on the above assumptions are:

\[
C_A(r, 0) = C_{A0} \text{ for } 0 < r < R'
\]

\[
C_A(R', t) = C_f
\]
where the system is initially kept at a constant uniform concentration, $C_0$, and particles surface are maintained at a constant core material concentration, $C_f$. Crank has derive the solution for this equation which was mentioned in Chapter 3 in Equation 3.1
Appendix C

Derivation of Relationship Between Bubble Initial and Final Radius

Due to the mass conservation balance, the final mass of the solid microbubble, $m_2$, plus the mass of the released hydrogen gas, $\Delta M_{H_2}$, is equal to the initial mass of the liquid particle, $m_1$. Therefore,

$$m_2 = m_1 - \Delta M_{H_2} \quad \text{(C.1)}$$

In order to solve this equation, we need to find a relationship between $M_{H_2}$ and $m_1$. Following this process reduces three parameters in equation C.1 to two parameters hence shows a relationship between $m_1$ and $m_2$. 7.1 provides enough information to find the mass of hydrogen as a function of total initial mass. Carbon mass is conserved while particles only release hydrogen. From 7.1 we know that:

$$\begin{align*}
\frac{N_{H_1}}{N_{C_1}} &= 1.01 \\
\frac{N_{H_2}}{N_{C_1}} &= 0.95
\end{align*} \quad \Rightarrow \quad \frac{N_{H_1} - N_{H_2}}{N_{C_1}} = 0.06 \quad \text{(C.2)}$$
where \( N_{H_1} \) shown the initial number of hydrogen molecules, \( N_{H_2} \) is the final number of hydrogen molecules, and \( N_{C_1} \) is the initial and final number of carbon molecules. To obtain the mass of hydrogen and carbon molecules, atomic masses for hydrogen and carbon are used. Therefore,

\[
\frac{m_{H_1} - m_{H_2}}{m_{C_1}} = \frac{\Delta M_{H_2}}{m_{C_1}} = \frac{0.06 \times 1}{12} \quad (C.3)
\]

Now, we can rewrite C.1 using C.3 which shows:

\[
m_2 = m_1 - m_{C_1} \times \frac{0.06 \times 1}{12} \quad (C.4)
\]

Assuming that hydrogen mass is only a small fraction of the total mass, we can approximately presume that \( m_{C_1} = m_1 \). Hence,

\[
m_2 = 0.995 \times m_1 \quad (C.5)
\]

According to literature the average density of the solid amorphous hydrogenated carbon produced from different hydrocarbons in plasma, \( \rho_2 \), is between 1.0 g/cm\(^3\) and 1.5 g/cm\(^3\) [240,241]. Assuming that the initial density of the liquid-like, \( \rho_1 \), particle can be estimated from toluene density which is 0.86 g/cm\(^3\) we can find a relationship between the initial radius and the final radius which is:

\[
\rho_2.V_2 = 0.995 \times \rho_1.V_1 \implies \rho_2.4.\pi.r_2^2.h = 0.995 \times \rho_1.\frac{4}{3}.\pi.r_1^3 \quad (C.6)
\]

where \( r_1 \) and \( r_2 \) are the initial and final radius of the bubble respectively and \( h \) is the thickness of the bubble shell. C.6 simply shows the relationship between \( r_1 \) and \( r_2 \) which is:
Here, we choose an average for the reported \( \rho_2 \) in literature which is 1.25 g/cm\(^3\) and use 0.86 g/cm\(^3\) for \( \rho_1 \). The final equation for \( r_1 \) as a function of \( r_2 \) which was used in Chapter 7 is

\[
r_1 = 0.603 \times r_2^{\frac{4}{3}} \tag{C.8}
\]
Bibliography


[175] J. M. Horn, J. Lightstone, J. Carney, and J. Jouet, “Preparation and charac-
terization of functionalized aluminum nanoparticles,” *AIP Conference Pro-

[176] K. W. Watson, M. L. Pantoya, and V. I. Levitas, “Fast reactions with nano-
and micrometer aluminum: A study on oxidation versus fluorination,” *Com-

[177] N. D. Tran, N. K. Dutta, and N. R. Choudhury, “Plasma-polymerized per-


[182] W. Nakao, H. Fukuyama, and K. Nagata, “Gibbs energy change of carbother-
mal nitridation reaction of al2o3 to form aln and reassessment of thermo-


Vita
Anaram Shahravan

Education
Ph.D. Chemical Engineering August 2012
The Pennsylvania State University, University Park, Pennsylvania, USA
B.S. Chemical Engineering May 2007
Sharif University of Technology, Tehran, Iran

Publications

Conference presentations
- “Dynamics of solid microbubbles formation,” AIChE, Minneapolis MN, October 2011.
- “Hydrophobic Nanoparticles for Nanofluids”, AIChE, Minneapolis MN, October 2011, Conference poster
- “Permeability Characteristics of Hollow Nanoparticles Fabricated by Low-Pressure Plasma Deposition,” ICOPS, Chicago IL, June 2011.
- “Charging of Finite Cylinders in Low Pressure Plasma”, ICOPS, Chicago IL, June 2011, Conference poster
- “Synthesis of Hollow Nanoparticles by Template Coating in Low-Pressure Plasma,” AIChE, Salt Palace Convention Center, Salt Lake City, Utah, November 2010.
- “Thin-Film Deposition on Nanoparticles and Nanowires In Low-Pressure Plasma,” AICHE, Philadelphia, PA, November 2008.
- “Thin-Film Deposition on Nanoparticles and Nanowires in Low-Pressure Plasma”, Gordon Conference, South Hadley, MA, July 2008.